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KONINKLIJKE AKADEMIE
VAN WETENSCHAPPEN
-:- TE AMSTERDAM -:-

PROCEEDINGS OF THE SECTION OF SCIENCES

VOLUME XI

JOHANNES MÜLLER :—: AMSTERDAM
: JULY 1909 :

(Translated from: Verslagen van de Gewone Vergaderingen der Wis- en Natuurkundige Afdeeling van 30 Mei 1908 tot 23 April 1909. Dl. XVII.)

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VOLUME XI

(— 1ST PART —)

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TE AMSTERDAM.

PROCEEDINGS OF THE MEETINGS
of Saturday May 30 and June 27, 1908.

(Translated from: Verslag van de gewone vergaderingen der Wis- en Natuurkundige Afdeeling van Zaterdag 30 Mei en Zaterdag 27 Juni 1908, Dl. XVII).

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Physics. — "*A contribution to our knowledge of the solarization phenomenon and of some other properties of the latent image*".

By A. P. H. TRIVELLI. (Communicated by Prof. S. HOOGEWERFF).

(Communicated in the Meeting of March 28, 1908).

I. *The image.*

In order to enquire into the density gradation a photographic plate may be exposed in two ways:

a. with constant light intensity and varying time of exposure;

b. by equal exposures, with different light intensities.

In order to eliminate the possibility of other circumstances being different, particularly those under which development is carried out, the first method has been adopted, a plate being divided into strips, and each succeeding strip receiving a longer exposure than the preceding one. This is combining several trial plates into one. In my opinion an "image" cannot be said to appear in this case; it only appears if the second method is adopted.

The results obtained by equal exposures with different light intensities I will call *copies*. A copy always shows an image, which may be positive or negative.

By a *normal* or non-polarized copy I understand copying positive-negative-positive- etc., which may be represented by

$$\pm \rightarrow \mp$$

By a *polarized* copy I understand copying positive-positive-etc. or negative-negative- etc., which may be represented by

$$\pm \rightarrow \pm$$

According to the investigations of WARNERKE[1]), W. ABNEY[2]), K. SCHAUM and V. BELLACH[3]), R. NEUHAUS[4]), and W. SCHEFFER[5]), the differences in density which appear in a photographic plate after exposure and development, may be ascribed to differences in the depth of the reduced silver haloid. So the image must have a plastic shape similar to that formed by the pigment-gelatine printing process, the insoluble part being a normal copy, the soluble part a polarized one (monochrome pinatypy).

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[1]) Phot. Archiv. 1881; S. 85 u. 119.
Phot. Mitt. Bd. 18; S. 65, 98 u. 285.
J. M. EDER, Handb. d. Phot. 1902; Bd. III; S. 106 u. 108.

[2]) J. M. EDER, Hand. d. Phot. 1902; Bd. III; S. 102.

[3]) Phys. Zeitsch. 1902; Bd. IV; S. 4.
J. M. EDER, Handb. d. Phot. 1903; Bd. III; S. 819.

[4]) Wied. Annal. d. Phys. u. Chem. 1898; Bd. 65; S. 164.

[5]) Phot. Chronik. 1904; S. 866.
Phot. Rundschau. 1904; S. 121.

It is characteristic of the normal copy, if exposed and developed normally that the portions where the density is greatest show a duller surface when seen by light reflected at an angle than the clearest portions. This is to be attributed to the presence of reduced silver-haloid grains immediately under the free surface.

If the image lies against the free surface, it may be called a surface image, in opposition to a "depth" image, with which this is not the case.

The cause of the appearance of the surface image has been ascribed by P. H. EYKMAN and myself[1]) to the surface tension of the wet gelatine. So a silver-haloid gelatine layer may be looked upon as consisting of a series of layers, of which the top one, i.e. the one at the free surface, is the most sensitive, while every succeeding one lying under it, is less sensitive. The exposure required to render a beginning of reduction by the developer visible, the liminal value ("Schwellenwert") consequently seems to increase in proportion to the depth; that of the topmost layer is equal to the liminal value of the plate itself. We will call this the "absolute", that of the succeeding layers the "relative" liminal value.

Leaving aside, for clearnes's sake, the mutual differences in sensitiveness of silver-haloid grains in one single layer, to which J. M. EDER[2]) and J. PLENER[3]) have drawn attention, the differences in size and shape and the topographic situation of the grains, the normal copy may be represented as is shown in cross section and graphically in fig. 1.

The shape of the image of a polarized copy might be represented as indicated in fig. 2. I have found that this explanation cannot be applied to a single photographic image, but it is applicable to chemigraphic processes, catatypy and the silver-pigmentgum process.

In the case of some polarized copies, as the counter-positive and -negative, a normal copy is developed first, the reduced silver haloid of which is dissolved and, after a diffused exposure, redeveloped. Now a depth image originates (fig. 3). Owing to the diffused exposure the base of it, leaving aside slight differences in light absorption, will everywhere be about equally distant from the free surface.

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[1]) Drude. Annal. d. Phys. 1907; Bd. 22; S. 119.

[2]) J. M. EDER, Handb. d. Phot. 1902; Bd. III; S. 64.
Phot. News. 1883; p. 81.

[3]) Phot. Korresp. 1882; S. 306.

According to the investigations of E. ENGLISH[1] and J. M. EDER[2] there are two images in the case of solarization. This question has not yet been satisfactorily cleared up, and a certain amount of confusion prevails as to the distribution of the normal and the polarized copy.

If the time of exposure, resp. the light intensity is increased, the reducibleness of the silver haloid increases in depth, finally to such a degree that provided the time of development be sufficient, the reduction extends to the glass, as is shown by the excellent microscopic preparations of W. SCHEFFER[3]. If solarization sets in, it will first occur in the apparently most sensitive layers, i. e. those at the free surface; consequently the reducibleness decreases from there, and on the time of exposure, resp. the intensity of the light being increased, it constantly extends further down. Thus an image is obtained as is graphically shown by fig. 4, from which it is at once apparent *that the solarized image is a normal copy and a surface image.* Under this image there is a polarized copy of greater density with *AB* for its base and from there to the glass there is a strip of fog, the density of which depends on the thickness of the emulsion.

That after all, in the case of solarization, the copy appears polarized, is therefore owing to the normal copy being of less density than the polarized one. It will, however, more or less reduce the contrasts and the wealth of detail. *It is consequently contrary to fact to understand polarization by solarization, as is always done.*

(In the figure the section of the solarized image is indicated by finer granulation, which is meant to show that the density has been reduced in that portion).

This at once accounts for the phenomenon occurring in the case of solarization of silver iodide gelatine discovered by LÜPPO-CRAMER[4]) and which points to the very rapid decrease in reducibleness of silver iodide when solarized.

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[1] Phys. Zeitschr. 1900; Bd. 2; S. 62.
J. M. EDER, Jahrb. f. Phot. u. Repr. 1902; S. 79.
Archiv. f. wiss. Phot. 1900; Bd. II; S. 260.

[2] Zeitschr. f. wiss. Phot. 1905; Bd. II; S. 340.
J. M. EDER, Handb. d. Phot. 1906; Bd. I; T. 2; S. 287.
Sitzungsber. d. Kaiserl. Akad. d. Wiss. zu Wien. Mathem-Naturw. Klasse; Bd. CXIV; Abt. IIa; Juli 1905.

[3] J. M. EDER, Jahrb. f. Phot. u. Repr. 1907; S. 81.

[4] I cannot omit quoting this experiment, which so clearly confirms the above: "Eine auffallende Erscheinung beobachtete ich endlich noch bei einem *Solarisierungsversuch* mit Jodsilbergelatine. Unter einem Negativ ergaben die Platten in "drei Sekunden bei diffusem Tageslicht ein ausexponiertes Bild. Eine sechs Stunden "lang unter demselben Negativ belichtete Platte schien sich in Amidolpottasche, "in welcher sie neben der drei Sekunden belichteten Platte entwickelt wurde, zuerst

II. *A few phenomena occurring with solarization accounted for by considering the form of the image.*

From the form of the image in fig. 4 it appears how impregnation of the silver-haloid gelatine plate with bichromate before exposure may influence the result obtained, which was pointed out by Bolas [1]). J. M. Eder and G. Pizzighelli [2]) attributed the result exclusively to hardening of the gelatine, by which development in the normal image is disturbed, and in which solarization acts hardly any part. It is evident that this image in the hardened gelatine more or less coalesced with the solarized image, in proportion to the strength of the bichromate solution employed, by which the development of the latter is suppressed to a greater extent and the polarized copy appears richer in contrast and detail. The fog, however, is not done away with.

While in the case of normal copies the latter may be removed with Farmer's reducer [3]), this treatment does not succeed in the case of polarization. The slight diffusion of this reducer discovered by W. Scheffer [4]), by which the action slowly progresses downwards from layer to layer, at once accounts for this phenomenon.

Of more significance to our knowledge of the latent image is the so-called neutralization of solarization by retarded development. That the said phenomenon is regarded as such is only attributable to the ideas of solarization and of polarization being confounded.

Development is retarded either by decreasing the amount of alkali

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"gar nicht zu reduzieren, während das kurz exponierte schon in allen Einzelheiten "erschienen war. Nach einiger Zeit merkt man indes, dass auch auf der überbelichteten Platte ein Bild vorhanden ist; dasselbe sitzt nur in den *tieferen Schichten* "allerdings als normales Diapositiv, d. h. noch nicht solarisiert während in der "Aufsicht erst nach längerer Entwicklung etwas zu sehen ist. Beim Fixieren merkt "man deutlich, dass *in der obersten Schicht* der lange belichteten Platte kein Bild "vorhanden ist, indem nach kurzem Fixieren das Bild auch in der Aufsicht kräftiger wird, offenbar weil das unreduzierte Jodsilber der obersten Schicht weggenommen wird". (J. M. Eder, Jahrb. f. Phot. u. Repr. 1903; S. 46. Zeitschr. f. wiss. Phot. 1903; Bd. I; S. 17).

[1]) J. M. Eder. Handb. d. Phot. 1902; Bd. III; S. 115.
Phot. News. 1880; Vol. 24; p. 304.

[2]) J. M. Eder. Handb. d. Phot. 1902. Bd. III; S. 115.

[3]) J. M. Eder. Handb. d. Phot. 1902 Bd. III; S. 555.

[4]) Brit. Journ, of Phot. 1906; p. 964.
J. M. Eder. Jahrb. f. Phot. u. Repr. 1907; S. 26.

in the developer or by the addition of potassium bromide. That only the rapidity of reaction of the developer is reduced, I was able to ascertain by the so-called neutralisation of solarization with a developer (rodinal 1 in 10) at a lower temperature. First a normal copy is developed, which when development is continued, turns into a polarized one.

However, the normal copy obtained in this way, differs very much from an ordinary one. When viewed by light reflected at an angle, it is just in the densest portions that the surface is found to have the highest gloss; consequently here the grains do not lie against the surface. After the copy has changed into a polarized one, in which the polarized depth image predominates, the surface remains unchanged, and now shows the highest gloss in the clear portions. Consequently the surface image has not undergone a reversion of density proportions, from which it follows *that the normal copy obtained by retarded development must be the solarized image*[1]). *This cannot be ascribed to a change of the solarization, i.e. to a change in the substance of the solarized latent image.*

Consequently in the surface glass we have a means of ascertaining in the case of solarization, whether an agent reacts upon the substance of the latent image or upon the development. Thus I could ascertain *inter alia*, that chromic acid mentioned by J. M. Eder [2]) and ammonium persulphate referred to by K. Schaum and W. Braum, which both exercise a hardening influence upon the gelatine, at the same time also react upon the substance of the latent image in the case of solarization, by which it is reduced to the substance of the ordinary latent image.

III. Sabatier's *polarization*.

If during the development of a plate light is admitted, three different phenomena may occur:

1. If a very slight amount of light is admitted, the plate in the developer shows an increase of reducibleness.

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[1]) It stands to reason that during the appearance of the normal copy in the developer, consequently before polarization sets in, development of the non-solarized silver haloid in the lower layers may take place. Consequently it is better to say that the solarized image is only formed within a certain definite time of development.

[2]) Phot. Korresp. 1902; S. 647.
J. M. Eder. Jahrb. f. Phot. u. Repr. 1903; S. 23.
J. M. Eder u. E. Valenta. Beiträge zur Photochemie. 1904; II; S. 168.
J. M. Eder. Handb. d. Phot. 1903. Bd. III; S. 828.

[3]) Phot. Mitt. 1902; S. 224.

2. If more light is admitted the image partly disappears, and a more or less fogged plate is obtained with partly a normal and partly a polarized copy, which shows great resistance to further development.

3. If still more light is admitted, the copy is polarized.

This last phenomenon I call SABATIER's polarization.

J. M. EDER [1]) credits SABATIER with first observing it, and says that SEELY gave the following explanation of it: The beginning of the development takes place at the surface; by the secondary exposure this developing image is copied upon the silver haloid underneath it, and as this exposure is more powerful than the first, the second image also develops more strongly, and total polarization results.

From the experiments carried out by me it appeared that the secondary exposure stopped the development of the surface image, for by reflected light it was seen that it did not increase in density any more, while total development of the whole surface might be expected. In order to ascertain to what extent the copying action of the developing surface image is operative in polarization, I effected the secondary exposure, at the advice of P. H. EYKMAN, on the glass side of the plate.

The exposed plate was developed for a short lime, and just after the appearance of the image it was, while still in the developer, covered with a piece of opaque, black paper, which was everywhere pressed tightly against the emulsion to prevent the formation of air-bells, from which uneven development might arise, and then the glass side was exposed to direct daylight. As the quantity of developer soaked up by the paper was small and the temperature was below the normal one, the plate, to save time, was put in the developer again in the dark room, great care being taken to prevent light from reaching the front of the plate. After fixation a polarized copy appeared.

This shows that the copying of the developing image at most acts a very secondary part in the appearance of polarization.

The latter can only be ascribed to the further development of the surface image being stopped, and to the reducibleness of the silver haloid underneath it being increased. Consequently here again two images are formed, one under the other: at the top a normal copy of little density, and under it a polarized one of greater density, corresponding to that of the polarized copy in fig. 3 in the case of solarization.

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[1]) J. M. EDER Handb d. Phot. 1898; Bd. II; S. 82.

The similarity between **Sabatier**'s polarization and solarization is so great, that R. **Lyle**[1]) attributed the phenomenon mentioned sub 2 to the first zero condition of **Janssen**'s periodicities of solarization being reached[2]). In one of my experiments it appeared to me that this similarity only existed in so far as no image was to be observed. The first zero condition is characterised by the maximum of density obtainable, whilst the plate in question remained very thin. Consequently the cause of the disappearance of the image cannot lie in this.

By transmitted light, too, the plate does not show polarization in the portions exposed most intensively by the primary exposure, but in the portions that received the smallest amount of light. (Therefore **Sabatier**'s polarization cannot be ascribed to solarization). It is easy to understand that the relative liminal value of a lower layer is first reached in those portions where the absorption of the surface image is the least, and where this layer, at the same time, is situated nearest to the free surface. So in this case the copying quality of the surface image exercises its influence.

IV. Herschel's effect.

By **Herschel**'s effect I understand polarization by double exposure. It differs from polarization by solarization in that much smaller amounts of light-energy are sufficient to produce it, and in the reducibleness of the primarily exposed silver haloid decreasing at once on a secondary exposure.

The duration of the primary exposure must always exceed the liminal value of the plate. After the secondary exposure has exceeded a certain maximum (*the critical exposure*), the plate shows a normal copy again. The value of the critical exposure depends entirely on the primary exposure. This has led to the so-called **Clayden**'s effect[3]) (black lightning) being looked upon as a new phenomenon of the photographic plate.

The first observation dates from 1839, and was made by J. **Herschel**, who stated that the red and the yellow rays of the spectrum could destroy the latent image of the blue and violet ones. At the same time a change in the degree of colour sensitiveness was ascertained. This was confirmed by CLAUDET [1]), H. W. VOGEL [2]), W. ABNEY [3]), P. VILLARD [4]) and R. W. WOOD [5]). E. ENGLISCH [6]), H. W. VOGEL and W. ABNEY, however, considered this phenomenon to be solarization. An experiment published by P. VILLARD clearly shows that in the case of very advanced exposures the critical exposure does not appear any more, and the whole phenomenon coalesces with solarization. The highest sensitiveness of the plate is manifested towards red, the lowest to green.

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[1]) Phot. Centralbl. 1902; S. 146.

[2]) Compt. rend. 1880; T. 90; p. 1447, T. 91; p. 199.
Moniteur de la Phot. 1880; p. 114.
Beibl. z. d. Annal. d. Phys. u. Chem. 1880; S. 615.
J. M. **Eder**, Handb. d. Phot. 1906; Bd. I; T. 2; S. 306 1898; Bd. II; S. 78.
J. M. **Eder**, Jahrb. f. Phot. u. Repr. 1894; S. 878.

[3]) J. M. **Eder** Jahrb. f. Phot. u. Repr. 1901; S. 610.
Camera Obscura. 1901; bldz. 513.
J. M. **Eder** Handb. d. Phot. 1906; Bd. I; T. 2; S. 812.
„ „ „ „ 1903; Bd. III; S. 834.

WARNERKE [7]) observed HERSCHEL's effect in images obtained by printing, and P. VILLARD, R. W. WOOD, R. LUTHER and W. A. USCHKOFF [8]) with Röntgen rays in the case of primary exposure. At the same time they demonstrated that the phenomenon did not appear if these exposures were reversed.

J. STERRY [9]) communicated another variety, viz. that certain kinds of chemical fog can be neutralized by weak light.

Some time ago one of my friends showed me a few camera exposures on EASTMAN films [10]), which I recognized as the phenomenon observed by J. STERRY. They had been exposed once, but had been in the camera for about 3 years without any precautions having been taken except that light had been prevented from reaching them. Consequently in this case the diffused exposure had been replaced by a chemical process of analysis, which had acted similarly, and had been exercised upon the silver bromide by the vapours given off by the celluloid, which had been diffused in the silver bromide gelatine.

Fig. 5 is an outdoor subject; it had a short exposure and shows various abnormalities. Nearly the whole copy is polarized, with the exception of the sky near *a*, where the critical exposure had been exceeded. The dogs in the foreground, reflecting the greatest amount of light there, show the beginning of the formation of a normal copy, and so do the shoulders of the female figure to the right, owing to which especially the left shoulder shows a false relief. Consequently the critical exposure is reached after the greatest transparency of the image has been obtained.

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[1]) Annal. d. Chimie et de Phys. 1848; 3e série; T. XXII.

[2]) H. W. VOGEL. Handb. d Phot. 1890; Bd. 1; S. 221.

[3]) Phot. Archiv. 1881; S. 120.

[4]) Soc. d'encourag. pour l'Industrie nation. Extr. d. Bulletin; Nov. 1899.

[5]) Astrophys. Journ. 1903; Vol. XVII; p. 361.

[6]) J. M. EDER. Jahrb. f. Phot. u. Repr. 1902; S. 73.

[7]) Phot. Arch. 1881; S. 120.

[8]) Phys. Zeitschr. 1903; S. 866.

[9]) This paper I only know from a resumé in J. M. EDER. Jahrb. f. Phot. u. Repr. 1903; S. 425.

[10]) The lens of the camera was a slow aplanat, and was used with full opening for the interior; for the outdoor exposure it was stopped down.

Between these beginnings of a normal copy and the polarized copy there is a clear strip, which is narrower where the exposure has been stronger. The dog to the left shows greater density of the normal copy than the one to the right, where the bright strip is broader. This strip occurs in the brighter parts in a manner that is the exact opposite of the way it occurs round the outlines of the leaves of the tree and of the bare trunk in the background ; a few shoots are even quite white. Here the strips are found in the darkest parts, and decrease in width towards the right of the tree top, round which a smaller light intensity has been active.

The wall was more strongly lighted to the left than to the right, and appears slightly darker there, but still it remains polarized, which is easier to see in the original film than in the reproduction. The left side of the tree top shows more halation than the right, while no halation whatever is to be seen in the part of the sky near *a*, which was subject to the action of light with greater contrasts. Here, however, one would have expected that halation would have acted in the opposite direction, viz. not decreasing in density in the darkest portions, but increasing in the lighter ones.

The comparatively slight density of the sky near *a* is striking, and so is the low colour sensitiveness to green (grass and foliage), while the dark blond and dark brown hair of the two female figures show a stronger action of the light, which can be seen better in the original copy. The wall in the background is white, so that here the colour sensitiveness to the red of the bricks cannot be ascertained

Fig. 6 renders the critical exposure still more strikingly. It represents an interior ; the film was exposed a few seconds, and shows every object in the room polarized, even a large portion of the halation owing to the light from the left window. What is seen outside through the windows has been copied normally ; here, consequently the critical exposure has been exceeded. The halation has partly made the lead setting of the coloured glass appear normal again, while to another portion it has given greater density owing to the action of the light being stronger. A large part of the right half and a smaller part of the left bottom section show differences in density, which must be ascribed to uneven action of the chemical reactions during the time the film was kept. Fig. 5 also shows this, but in a slighter degree ; here, however, it is less noticeable on account of the wealth of detail of the image. The action being slighter to the right, the images are seen to be thinner accordingly.

The same thing is to be observed in a Röntgenogram placed at my disposal by P. H. EYKMAN. The plate was exposed to Röntgen rays with a so-called intensification screen (calcium wolframate screen), and laid aside some time before development. Calcium wolframate postluminesces [1]) owing to which a plate is consequently further exposed. The objects photographed with Röntgen rays were a piece of bone, a piece of thin and a piece of thicker, insulated copper wire. Fig. 7 gives a reproduction of the negative. The places of the thin copper wire show development of the silver bromide which is nearly as strong as in the field, where the Röntgen rays and the luminescence together have acted most strongly. A narrow strip along the edge indicates how far the screen covered the plate; consequently there only the R. rays have acted. The place of the thin copper wire does not show a trace of development there; consequently the exposure remained below the liminal value.

The development of this place cannot be put down to irradiation through the screen; in that case the same thing would have to be observed in the case of the thick copper wire and the edge of the screen. Consequently the R rays must really have acted in such a way in that place, that the screen luminesced and this acted upon the silver bromide, while the exposure to R. rays remained below the liminal value.

P. H. EYKMAN also showed me a negative in the case of which the screen after irradiation had only been brought into contact with an unexposed plate [2]). It showed a very thin image, from which it follows that the strongest action of the screen takes place immediately after the transformation of the absorbed Röntgen energy. Consequently if in the case of a röntgenogram with a calcium wolframate screen the action of the R. rays could be prevented, much shorter exposures would be sufficient to produce a good image. Hitherto this has proved to be impossible.

Another fact important for our knowledge of the latent image may be gathered from fig 6. The right bottom corner shows that the thinner the fog of diffused exposure becomes, the thinner also the polarized copy is. From this it follows *that in the case of secondary exposure the liminal value is lower than in the case of primary exposure, i.e. the amount of light necessary to effect the begin-*

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[1]) Fortschr. a. d. Geb. d. R-Str. 1901; Bd. IV; S. 180.

[2]) The calcium wolframate screen was exposed to the R rays at the same time as the negative of Fig. 7.

ning of a decrease in reducibleness is smaller than is necessary for a beginning of an increase of this power with the original condition of the silver bromide.

V. *The theory of the latent image.*

In the case of the theory of the latent image two facts have to be observed, which are directly connected with each other:

1. The action of the light upon the silver haloids;
2. The physical or the physical and chemical changes in the silver haloid resulting from this action.

The theory proper of the latent image is only restricted to the latter, consequently comprises only secondary phenomena. Of all the theories enunciated, only the subhaloid theory of CHOISELAT and RATEL [1]) has maintained itself, especially owing to the subsequent investigations of M. CAREY LEA [2]), H. WEISS [3]), J. M. EDER [4]), and others. While J. M. EDER [5]) looks upon silver subhaloid as a molecular compound, M. CAREY LEA [6]), E. BAUER [7]), L. GUNTHER [8]), and LÜPPO-CRAMER [9]), consider it an absorption compound of colloidal silver and silver haloid, thus practically maintaining ARAGO's old silver-germ theory in a new shape. However, it is impossible yet to point out a single fact in photography from which it appears which of these two theories is to be preferred; all chemical reactions on the latent image might be accounted for by either theory and neither of them has hitherto afforded a definite explanation of the various photographic phenomena.

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[1]) Compt. rend. 1843: T. 16; Nr. 25.
" " " T. 17; Nr. 4.
J. M. EDER. Handb. d. Phot. 1898; Bd. II; S. 111.

[2]) Americ. Journ. of Science. 1887; Vol. 33; p. 349.
Phot. Korresp. 1887; S. 287, 344 u. 371.

[3]) Zeitschr. f. phys. Chemie 1905; Bd. 54; S. 305.
Chem. Centralbl. 1906; Bd. I; S. 807.
J. M. EDER. Jahrb. f. Phot. u. Repr. 1906; S. 473.

[4]) Sitzungsber. d. kaiserl. Akad. d. Wiss. zu Wien. Mathem.-naturw. Klasse. Bd. CXIV; Abt. IIa; Juli 1905.
Zeitschr. f. wiss. Phot. 1905; Bd. III; S. 329.
J. M. EDER. Handb. d. Phot. 1906; Bd. I; T. 2; S. 277.
Phot. Korresp. 1905; S. 425 u. 476.
" " 1906; S. 81, 134, 181 u. 231.
" " 1907; S. 79.

[5]) See note 4.

[6]) See note 2.

[7]) Zeitschr. f. phys. Chemie. Bd. 45; S. 618.

[8]) Abhand. d. naturk. Ges. Nürnberg. 1904; Bd. 15; S. 26.

[9]) Phot. Korresp. 1906 u. 1907.
LÜPPO-CRAMER. Photogr. Probleme. 1907; S. 193.

As the photo-chemical process of analysis upon the silver haloid is only characterized by a continuous reduction process, it is quite natural to assume this also in the cases of the solarized latent image Still there are a few phenomena which seem to contradict this.

Thus W. ABNEY [1]) assumed the formation of an oxybromide, and founded this assumption on the fact observed that potassium bichromate and potassium permanganate, perhydrol and a few anorganic acids promote solarization. The anti-solarizing action, also pointed out by him, of reducing agents, like pyrogallol, ferrous sulphate, ferrocyanide of potasium, nitrites, and sulphites, has only been judged from the appearance or non-appearance of polarization, and may be entirely reduced to retarded development.

LÜPPO-CRAMER [2]) considers the oxidation theory of solarization absurd. He points to the solarization of the plate even if no oxygen is admitted, and to the circumstance that all the agents that prevent solarization, are halogen-absorbing substances. As a characteristic example he mentions silver nitrate, the anti-solarizing action of which is, according to him, to be ascribed to halogen-absorption, not to oxidation, and considers this action analogous to that of nitrites, sulphites and hydroquinone.

This view is at variance with his criticism of the oxidation theory, in which he also points to the continuous loss of halogen in the case of continued exposure of the silver haloid, and to his observation that a bromide solution counteracts solarization, and may even entirely neutralize the latent image[3]). *Consequently halogen-absorption must promote solarization.* The promotion of solarization mentioned by W. ABNEY, and referred to above is not to be ascribed to oxidation, but to halogen absorption.

That oxidation of the substance of the latent image neutralizes solarization, has been ascertained by J. M. EDER [4]) with his chromic acid reaction, and by K. SCHAUM and W. BRAUN [5]) with their ammonium persulphate reaction. That in this case we really have not the phenomenon of retarded development I could observe through the formation of a dull surface image. Further LÜPPO-CRAMER[1]) proved that the silver subhaloid of POITEVIN's photochromics undergoes regression to silver haloid by oxidation. J. M. EDER[2]) described the same thing in his investigations of the latent image with the nitric acid reaction.

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[1]) Proc. Roy. Soc. 1873; Vol. 27; p. 291 a. 451.

[2]) LÜPPO-CRAMER. Phot. Probleme. 1907; S. 138.

[3]) J. M. EDER, Jahrb. f. Phot. u. Repr. 1902; S. 481.

[4]) Phot. Korresp. 1902: S. 647.
J. M. EDER, Jahrb. f. Phot. u. Repr. 1903; S. 23.
J. M. EDER, u. E. VALENTA, Beiträge zur Photochemie. 1904; II; S. 618.
J. M. EDER, Handb. d. Phot. 1903; Bd. III; S. 828.

[5]) Phot. Mitt. 1902; S. 224.

Quite a different view of the progressive photochemical analysis of silver haloids, was given by H. LUGGIN[3]). He stated that in the case of more intensive exposure, also a proportionately greater amount of formed silver haloid, under the influence of the increasing halogen pressure takes from the silver haloid the power of affording germ-points for the deposit of metal, and that consequently halogen-absorbents (chemical sensitizers) would be the best means of keeping the halogen pressure as low as possible, and so of preventing solarization. Consequently he considers solarization as a phenomenon consisting in the prevention of germ-formation. His statement: "The beginning of solarization may often be obviated by selecting smaller stops and increasing the exposure accordingly," is confirmed in the case of silver iodide gelatine[4]).

Still this proposition that halogen absorption prevents solarization is at variance with what goes before. I have therefore investigated this matter more closely.

Silver haloid is decomposed by the action of light, but a polished silver bar exposed in the light to halogen vapours, at once combines with it to form halogen silver. Consequently in the presence of an excess of halogen the silver haloid is not decomposed.

A highly sensitive silver bromide gelatine plate, which was partly coated with collodion, was exposed to direct daylight. It was observed that the photo-chemical decomposition under the collodion remained considerably behind that of the free surface, and had not even increased appreciably after an exposure of several weeks. The violet brown discolouration appeared only at the free surface, and could be removed by the plate being rubbed carefully. A plate, exposed at the same time on the glass side, also showed retardation as to the photo-chemical decomposition process, and against the glass the silver bromide seemingly remained unaltered. Consequently the fact that halogen prevents diffusion counteracts decomposition. In the case of an excess of liberated halogen the opposite reaction takes place, which is quite in accordance with the regression of the latent image by a bromide solution in the case of silver bromide, as found by LÜPPO-CRAMER.

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[1]) Phot. Korresp. 1907; S. 489.

[2]) See note 4, p.

[3]) J. M. EDER, Jahrb. f. Phot. u. Repr. 1898; S. 162.

[4]) J. M. EDER, Handb. d. Phot. 1906. Bd. I; T. 2; S. 309. LÜPPO-CRAMER, Phot. Probleme. 1907; S. 152.

The diffusion of liberated halogen will always take place in a smaller degree in the series chlorine, bromine, iodine, on account of the atomic weight rising.

H. LUGGIN's rule must, therefore, be modified to the effect that in the case of a certain definite light intensity the progressive and regressive reduction get into a condition of equilibrium, which is only got over by a loss of halogen (absorption by the chemical sensitizer and diffusion).

The same thing was said in other words before now by J. PRECHT [1]), but on the ground of the appearance of solarization.

With this modified proposition of H. LUGGIN the deviations [2]) from R. BUNSEN's and H. ROSCOE's reciprocity rule [3]) can be accounted for, to which also belong the phenomena in the case of silver iodide gelatine just mentioned.

The knowledge of the latent image is arrived at by development. While the exposure causes decomposition of the silver haloid accompanied by a quantitative increase in silver subhaloid, a decrease of reducibleness appears during development after a certain maximum of exposure. The solarization phenomenon is, therefore, a development phenomenon in the sense that development, owing to the modified properties of the latent image, shows a change.

Consequently in order to account for solarization a knowledge of the nature of development is requisite. Without it solarization remains an unsolvable problem.

Two methods of development are distinguished: The physical and the chemical method [4]). Physical development is characterized by a deposit of a reduced silver compound from the developer on the exposed silver haloid; chemical development by reduction of the exposed silver halogen itself.

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[1]) Zeitschr. f. wiss. Phot. 1905. Bd. III; S. 75.

[2]) J. M. EDER, Handb. d. Phot. 1906; Bd. I; T. 2; S. 48 u. 49.
„ „ „ „ 1902; Bd. III; S. 228.
„ „ „ „ 1898; Bd. II; S. 3 u. 5.
Phot. Mitt. 1890; S. 261.
Proc. Roy. Soc. 1893; Vol. 54; p. 143.

[3]) POGGENDORF Annal. d. Phys. 1862; Bd. 117; S. 538.

[4]) J. M. EDER, Handb. d. Phot. 1898; Bd. II; S. 29.
„ „ „ „ 1906; Bd. I; T. 2; S. 250.

By W. Ostwald 1), K. Schaum and W. Braun 2) it was supposed that the reduction of the silver bromide with chemical development was in the first instance brought about by a minimum amount of silver bromide dissolving as positive silver- and negative haloid-ion, after which the reduced substance was precipitated upon the germs. Lüppo-Cramer 3) succeeded in showing that a number of developing processes which were formerly looked upon as being purely chemical in their nature, not only in reality proceed physically, but that every chemical development is also partly of a physical character. W. Scheffer 4) was the first to show by a microscopical investigation that the entire chemical development is physical in its nature, i.e. it is brought about by molecular attraction between the photochemically reduced silver haloid, the germ, and the reduced feeding-substance. This, consequently, accounts for the altered structure of the exposed silver bromide gelatine plate before and after development 5).

Still the development of the photographic plate by the so-called chemical method really shows a difference from the physical method. Lüppo-Cramer 6) succeeded in demonstrating that the substance of the image in the case of a negative developed by the so-called chemical method, still contained bromine by the side of ordinary silver, which bromine he supposed to be a constant solution of silver in silver bromide. From this he infers that during the development, beside the silver another intermediate product must originate. It is only natural to assume, on the analogy of the reduction process of the silver haloid to silver through subhaloid, that also in the case of so-called chemical development the reduction takes place in the same way. Thus it appears that between chemical and physical development there is only this difference that the former keeps the subhaloid in solution with more difficulty than the latter, owing to which perfect reduction cannot take place. This at the same time accounts

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1) W. Ostwald. Lehrb. d. allgem. Chemie. 1893; Bd. 2; S. 1078

2) J. M. Eder. Jahrb f. Phot. u. Repr. 1902; S. 476.
Phot. Mitt. 1902; S. 229.

3) Lüppo-Cramer. Phot. Probleme 1907. S. 159.

4) Phot. Rundschau 1907; S. 142.
Phot. Korresp. 1907; S. 384.

5) S. E. Sheppard and C. E. K. Mees. (Zeitsch. f. wiss. Phot. 1905; Bd. III; S. 356) consider V. Bellach's observation that the size of the grain of the developed image decreases during the drying of the emulsion, to be in accordance with G. Quincke's foam structure theory of the silver haloid grains which, according to him, contain gelatine. The non-coalescence of the exposed with the developed grain shows the incorrectness of this view.

6) Phot. Korresp. 1906 S 819

for the fact that the image developed with certain developers loses density in the fixing bath; this loss of density is analogous to what is observed in the case of P. O. P. papers with silver chloride.

This further explains another apparent contradiction. While with silver chloride a lower and with silver bromide a higher degree of sensitiveness to light is observed, in other words, while quantitatively the same photochemic decomposition of silver bromide takes place with less absorption of light energy than in the case of silver chloride the exact opposite is seen to take place with the increase in density during development, which has been pointed out by H. and R. E. LIESEGANG [1]), KÖNIG [2]) and LÜPPO-CRAMER [3]). Considering that silver chloride possesses a higher solubility, resp. has the power of bringing a greater number of ions into solution than silver bromide, it is easy to understand that quantitatively reduction can take place in a larger measure per unit of time, notwithstanding silver chloride is a more constant compound than silver bromide.

With silver iodide the same thing is observed still better. The reducibleness, resp. solubility is still less in this case, which has often occasioned the unjustified conclusion, that silver iodide is less sensitive to light than silver bromide, while the exact opposite is observed in the case of daguerreotypy and the wet collodion process, since here the feeding substance for development is introduced from without. Accordingly LÜPPO-CRAMER could use with silver iodide developers like amidol potassium carbonate, triamidophenol, diamidoresorcin, and triamidoresorcin, which show a far too great rapidity of reaction for silver bromide plates.

The higher sensitiveness of silver iodide-bromide plates as compared with silver bromide plates, owing to which more detail can be obtained in the darkest parts of the image, may therefore be ascribed to the more rapid formation of germs in the case of silver iodide, while the silver bromide serves as feeding substance for the developer. This further appears from the optical sensitizing of silver iodide-bromide plates.

While silver bromide can easily be made colour sensitive, this is not the case with silver iodide, which has been pointed out by J. M. EDER [4]), LÜPPO-CRAMER [5]), and others. Still both may be dyed by optical sensitizers, but in this case the silver iodide-bromide plate behaves more like a silver iodide plate.

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[1]) Phot. Mitt. 1901; S. 362.
Phot. Wochenbl. 1901; S. 405.
J. M. EDER. Jahrb. f. Phot. u. Repr. 1902; S. 572.

[2]) Phot. Korresp. 1903; S. 14.

[3]) J. M. EDER. Jahrb. f. Phot. u. Repr. 1903; S. 401.

[4]) J. M. EDER. Handb. d. Phot. 1906; Bd. I; T. 2; S. 269.

[5]) J. M. EDER. Jahrb. f. Phot. u. Repr. 1903; S. 46.
" " " " " " 1904; S. 390.
Zeitschr. f. wiss. Phot. 1903; Bd. I; S. 17.

At the 79th German Physical and Medical Congress held in Dresden in 1907 W. SCHEFFER[1]) communicated a solarization theory founded upon his microscopic investigations[2]), which explains solarization in quite a simple way.

When the exposed silver bromide gelatine plate is being developed certain grains ("Ausgangskörner") send out germs, upon which the reduced substance is deposited, because other grains ("Nahrkörner", formerly called "Lösungskörner") are dissolved in the developer and cause the growth of the germs. In an overexposed emulsion too many germ-producing grains "explode", and an insufficient number of "feeding" grains remain, so that no image of sufficient density can be formed. Consequently this theory is founded upon the transition of "feeding" grains into germ-producing ones by exposure, or rather of silver haloid into silver subhaloid.

This theory cannot be reconciled to the fact found by J. STERRY[3]), J. M. EDER[4]) and LÜPPO-CRAMER[5]), that solarization can also appear with primary fixation, for in this case the feeding substance is supplied from without. The same holds good with regard to daguerreotypy.

B. HOMOLKA's solarization theory[6]) : "In the decrease of the amount of silver bromide I recognize the primary cause of solarization", is irreconcilable to the above, not to mention the circumstance that these two theories cannot explain the second reversion of solarization, and cannot account for the fact that even with the strongest overexposures an excess of silver haloid, i. e. of feeding substance, can be proved to be still present in the emulsion.

From the solarization with primary fixation it therefore appears, that the silver haloid germ loses this germinating property on further exposure, i. e. through the continued photochemical decomposition it has passed into another subhaloid containing less halogen, which possesses no germinative property. O. WIENER[7]) proved the possibility of the existence of more subhaloids. Let us call the first the α-silver subhaloid and the second the β-silver subhaloid.

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[1]) Phot. Korresp. 1907; S. 487.

[2]) Phot. Rundschau. 1907; S. 65 u. 142.
Phot. Korresp. 1907. S. 233 u. 384.

[3]). J. M. EDER. Jahrb. f. Phot. u. Repr. 1899; S. 289.

[4]) J. M. EDER. Handb. d. Phot. 1906; Bd. I; T. 2; S. 312.

[5]) LÜPPO-CRAMER. Phot. Probleme, 1907; S. 150.

[6]) Phot. Korresp, 1907; S. 168.

[7]) J. M. EDER. Jahrb. f. Phot. u. Repr. 1896; S. 55.

The reappearance of reducibleness in the case of continued exposure, the so-called second reversion of solarization might then again be attributed to a newly formed γ-silver subhaloid, or, as the third reversion has not been observed, to a metallic silver germ or what is also possible, to both.

It must be emphasized at the very outset, that it is by no means impossible that before the α-silver subhaloid one or more other subhaloids, richer in halogen, are formed, which possess no germinative property, for a primary exposure below the liminal value of the plate points to photochemical decompositions taking place through the occurrence of auto-sensitizing[1]), so that the liminal value cannot be considered identical with the photochemical induction. Nor must it be inferred from the above that the α- or the β-silver subhaloid does not consist of more than one silver subhaloid.

Consequently it appears from all this that sensitiveness to light and reducibleness must on no account be identified, as is generally done.

The untenableness of the existing theories of HERSCHEL's effect by CLAUDET, P. VILLARD, R. W. WOOD and WARNERKE is accounted for by this faulty identification of reducibleness with sensitiveness.

For the appearance of HERSCHEL's effect it is necessary that the primary exposure should exceed the liminal value of the plate. Consequently α-silver subhaloid must have been formed.

That by the secondary exposure a regressive reaction occurs between the α-silver subhaloid and halogen, cannot be assumed, because in the case of prolonged exposures HERSCHEL's effect coalesces with solarization, in connection with which the formation of the β-silver subhaloid without germinative property has already been stated. The experiments of W. ABNEY mentioned above, also prove that halogen absorption promotes the phenomenon. Consequently the secondary exposure acts in such a way that the α-silver subhaloid formed photochemically by the first exposure is reduced to β-silver subhaloid more rapidly than it has been possible for *an equal quantity* of α-silver subhaloid to be formed afresh. (In this case it may happen that the silver subhaloid has already entirely been photochemically dissolved, before the silver haloid has been able to supply it). This appears from the discussion of fig. 6. The photochemical induction of the α-silver subhaloid is, therefore, lower than the liminal value of the silver haloid. *Consequently the α-silver subhaloid is a substance of greater sensitiveness to light than the silver haloid.*

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[1]) Vide: J. M. EDER. System der Sensitometrie phot. Platten. Sitzungsber. d. kais. Akad. d. Wiss. in Wien 1899; IIa; Bd. 108; S. 1407. J. M. EDER u. E VALENTA. Beiträge z. Photochemie. 1904; Bd. II; S. 48.

If with the secondary exposure the amount of α silver subhaloid originally present is exceeded, a normal copy is obtained again. The critical exposure, therefore, is that secondary exposure by which the same amount of α silver subhaloid is formed as was present after the primary exposure. So the best gradation of the polarized copy in the case of Herschel's effect is obtained, if lower light intensities are employed, as is shown by experiments.

The amended proposition of H. Luggin states that with a certain definite light intensity the progressive and the regressive reaction in the silver haloid arrive at a state of equilibrium, if the liberated halogen is not removed. This removal of halogen, either by diffusion or by chemical sensitizers, is therefore of paramount influence upon the origination of Herschel's effect. Consequently the most successful experiment is obtained with an emulsion which immediately absorbs the liberated halogen, or what is better even, if between the primary and the secondary exposure the plate is put aside for a considerable time, by which the liberated halogen is diffused out of the emulsion. It is still simpler to treat the plate after the primary exposure with a halogen absorbent, as was done by W. Abney, and we therefore regard judson blue, mentioned by H. W. Vogel[1]) as a substance probably behaving analogously.

Therefore the direct decomposition of the silver haloid by reducers as in the case of J. Serry's experiments and fig. 5 and 6, in which the liberated halogen enters into combination, acts so favourably upon Herschel's effect.

This makes P. Villard's statement clear that not all emulsions are equally suitable for experiment, as in the various emulsions there are different chemical sensitizers (both in quality and in quantity).

At the same time the nature of the phenomena in the case of intermittent exposure becomes clearer now.

That the effect of development upon silver bromide gelatine (but not necessarily the photochemical decomposition) is always slightly less than with a continuous exposure of the same duration was observed by W. Abney[2]), K. Schwarzschild[3]), and others. Many beginners in photography have observed the same thing when having made two exposures of different objects on the same plate. In this case it is easy to observe that not the sum of the two images is obtained, but that in one place one object dominates, in another place the other object.

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[1]) H. W. Vogel. Handb. d. Phot. 1890; Bd. I; S. 221.

[2]) Photography 1893; p. 682.
Phot. Archiv. 1893· S. 339.
J. M. Eder. Jahrb. f. Phot. u. Repr. 1894; S. 378.

[3]) Phot. Korresp. 1899; S. 171.

According to K. SCHWARZSCHILD the result in the case of the exposure being intermittent depends, *inter alia*, upon the relation between the interval and the duration of the separate exposures; the longer the interval the better opportunity the halogen has of escaping by diffusion, or of being absorbed by a chemical sensitizer, and the more readily the next exposure will photochemically decompose the α silver subhaloid germ, which is more sensitive to light than the silver haloid, into β silver subhaloid and halogen, owing to which the result of development, apart from the photochemical induction which is to be exceeded again, will remain below the sum of the components.

The difference in sensitiveness to light between silver haloid and the α silver subhaloid appears, according to the above experiments, to depend largely upon the kind of light with the seconday exposure. The less sensitive the silver haloid and the more sensitive the α silver subhaloid is to a given colour, the more pronounced Herschel's effect will be. The smaller this difference, the more rapidly the silver haloid will produce fresh α silver subhaloid germs; it is true, in this case polarization is observable, but the minimum reducibleness is soon reached. Further this is, of course, also dependent upon the amount of α silver subhaloid, i. e. upon the duration of the primary exposure. Perfect neutralization of reducibleness need not occur then.

Consequently the colour sensitiveness occurring in the case of HERSCHEL's effect is to be ascribed to the colour sensitiveness of the α silver subhaloid. Not one of the theories of the latent image enunciated hitherto can account for the phenomenon in such a simple way as the subhaloid theory. The subhaloids are dyes of quite different colours from silver haloid, and consequently with quite different spectra, owing to which the possibility exists of quite different colour sensitiveness, as in fact actually appears from the experiments of O. WIENER [2]).

P. VILLARD proved spectroscopically that the greatest dlfference between the liminal value of the silver haloid and the photochemical induction of the α-silver subhaloid is situated in the red

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[1]) Probably these photochemical decompositions proceed according to an exponential formula.

[2]) J. M. EDER. Jahrb. f. Phot. u. Repr. 1896; S. 55.

and consequently that the α-silver subhaloid is a substance sensitive to red. If α silver bromide gelatine plate is exposed to the action of a continuous spectrum, the reducibleness in the case of increasing exposure will proceed from blue to red. While after development it is observed that with increased exposure the density of the plate increases about and in the spectral blue, the yellow, the orange, and especially the red obtain only very slight densities. Consequently it is evident that the cause why the density of the image in the red, yellow, and orange portions cannot increase above a maximum, which is very low, lies in the α silver subhaloid possessing a far greater sensitiveness to red than the silver haloid, so that very soon a state of equilibrium has been reached, in which in a progressive process as much α-silver subhaloid is formed as destroyed.

The substance of the developable latent image is considered identical with M. CAREY LEA's photohaloid. Now how does this behave in red light?

M. CAREY LEA[1] exposed his pink photohaloid to the action of a spectrum; while under all colours the photohaloid changed, it remained unchanged in the red. From this it appears that the subhaloid germ of the latent image must be another substance than M. CAREY LEA's photohaloid.

The behaviour of Röntgen rays differs from that of other kinds of light. According to P. VILLARD, R. W. WOOD, R. LUTHER, and W. A. USCHKOFF they show no HERSCHEL's effect in the case of secondary exposure. This cannot be ascribed to total non-sensitiveness of the α silver subhaloid to Röntgen rays. It is true, F. HAUSMANN[2] and others stated that Röntgen rays produced no solarization, and consequently that there was no formation of β silver subhaloid, but P. H. EYKMAN[3], and subsequently K. SCHAUM and W. BRAUN[4] could show that they do. So the silver subhaloid is also sensitive to Röntgen rays, and the non-appearance of HERSCHEL's effect must be put down to the cause that for Röntgen rays the silver haloid has a liminal value as great as, or greater than the photochemical induction of the α silver subhaloid. It is therefore assumed that in the case of röntgenography the intermittent exposure, apart from the photographic induction to be exceeded each time, does not produce a photographic effect that remains below that of a continuous irradiation.

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[1] Americ. Journ. of Science 1887; Vol. 33; p. 363.

[2] Fortschritte a. d. Geb. d. R.-Str. 1901; Bd. V; S. 89.

[3] Fortschr. a. d. Geb. d. R-Str. 1902, Bd. V, Heft 4.

[4] Zeitschr. f. wiss. Phot. 1904; Bd. I; S. 382.

From H. Luggin's modified proposition it appears clearly, how the chemical sensitizers promote the photochemical decomposition process of the silver haloids by halogen absorption. They consequently prevent regression.

Lüppo-Cramer [1]) describes the following experiment, which confirms this. Precipitated silver chloride shows neither with silver nitrate, nor with ammonia, both chloride absorbents, any increased sensitiveness to light when photochemically decomposed; in an emulsion where the rapid escape of the liberated halogen is prevented, the action of the chemical sensitizer is therefore observed. From this it follows that the chemical sensitizer does not react upon the silver haloid itself at all.

Even from the considerable deviations from the reciprocity rule in a silver bromide gelatine plate with very low light intensities it follows that gelatine is not a chemical sensitizer, which has also been proved in another way, experimentally, by Lüppo-Cramer.[2])

While the chemical sensitizers act very favourably in the printing-out process, they have no, or even a detrimental influence in the case of silver haloid emulsions intended for development, as has been pointed out by Lüppo-Cramer [3]). If it is borne in mind that the α silver subhaloid germ itself is a substance very sensitive to light, which with loss of halogen, passes into the β zilver subhaloid without germinative property, it is clear that a too active chemical sensitizer does not promote reducibleness.

A number of chemical sensitizers, however, are oxidizers at the same time. From what has been said above it has appeared that oxidation transforms the β silver subhaloid into α silver subhaloid (neutralization of solarization), which may be thus represented: β silver subhaloid + oxygen = silver oxide (Ag_2O ?) + α silver subhaloid.

This reaction seems to proceed very slowly in the case of subbromides.

Owing to this complications may arise, so that the chemical sensitizer, while on one hand promoting the photochemical reduction, on the other hand again partly oxidizes the silver subhaloid that has been formed. Here the action of the chemical sensitizer is favourable for the process of development, as in the case of the silver iodide collodion plate with silver nitrate, which in the presence of light is a powerful oxidizer [1]), and the question is whether the so-called neutralization of solarization by silver nitrate is not to be ascribed to this as well, and consequently is real neutralization.

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[1]) Phot. Korresp. 1901; S. 224.
Lüppo-Cramer. Wissensch. Arbeiten 1902; S. 87.
J. M. Eder. Jahrb. f. Phot. u. Repr. 1906; S. 648.

[2]) Lüppo-Cramer. Phot. Probleme. 1907; S. 33.

[3]) Phot. Korresp. 1903; S. 25.

If silver haloids are allowed to be photo-chemically decomposed, the great influence of the size of the grain at once becomes evident. While fine grain silver chloride or bromide is decomposed rapidly, the latter even more rapidly than the former, the directly visible decomposition in the case of course-grain silver haloids is slower. This can at once be accounted for by H. LUGGIN's modified rule. At the surface of the silver haloid grain the liberated halogen can escape more easily, or enter into composition; inside the grain it acts regressively, so that the progression will decrease from the surface to the centre.

H. LUGGIN [2]), too, refers to the same thing in the case of silver iodide. But even if it is in a very finely divided condition, the directly visible photo-chemical decomposition does not take place rapidly. Owing to its greater atomic weight the liberated iodine not only diffuses more slowly, but moreover it is a solid substance. By absorption of this iodine, e. g. by silver nitrate, the directly visible photo-chemical decomposition at once becomes more rapid, so that it is clear why a silver haloid which is more sensitive may all the same yield a less advanced photo-chemical decomposition.

The surface decomposition of the silver haloid grain at the same time points to the fact that here, too, the seat of the latent image is to be looked for. This is also to be inferred from further data. Thus the deposits of reduced silver haloids discovered by W. SCHEFFER [3]) always start from the surface of the silver haloid grain, which appears from a microphotograph published by him. Further LÜPPO-CRAMER [4]) pointed to the dependence of the quantity of dye in the case of optical sensitization upon the surface to be coloured (i. e. upon the size of the grain) with silver chloride and silver bromide.

When it has been pointed out that in the appearance of solarization by primary fixation and secondary development the existence of a silver subhaloid can be proved, this is not enough to account for the solarization phenomenon.

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[1]) M. CAREY LEA (Phot, Korresp. 1887; S. 346) and LÜPPO-CRAMER (Phot. Korresp. 1907; S. 538) showed that silver subiodide is a substance which is extremely easily oxidized.

[2]) Zeitschr. f. phys. Chemie. 1897; Bd. 23; S. 611.

[3]) Phot. Rundschau. 1907; Heft 6.

[4]) J. M. EDER. Jahrb. f. Phot. u. Repr. 1902; S. 58.
" " " " " " 1905; S. 61.

In order to illustrate this let us assume a photo-chemical decomposition with direct recomposition of the liberated halogen.

If the exposure of a photographic plate is prolonged, the silver haloid will keep forming α silver subhaloid, which is the germ for development. From HERSCHEL's effect, however, it appears that this α silver subhaloid in itself is a highly light-sensitive compound, so that it is not to be assumed that a continual accumulation of germs is taking place. Consequently the α silver subhaloid rapidly decomposes into β silver subhaloid and halogen. At the surface of the silver haloid grains a condition therefore arises in which the number of germs present depends upon formation and destruction.

If the quantity of the remaining grain surface silver subhaloid decreases, the quantitative formation of α silver subhaloid will also decrease, and as the latter itself is highly sensitive to light, the consequence of this will also be a quantitative decrease of the number of remaining germs, in other words, the reducibleness will decrease, i. e. solarization will set in.

This phenomenon is, therefore, entirely dependent upon the available surface of the grain (size of the grain). In his experimental researches LÜPPO-CRAMER [1]) repeatedly pointed to this fact.

In reality this, of course, does not take place so rapidly. The various makes of plates have chemical sensitizers which differ from each other (qualitatively and quantitatively). This, together with the prevention of diffusion, is the reason why the different commercial plates begin to get solarized after mutually different exposures.

The thiosulphate reaction shows peculiarities which can be accounted for now. The subhaloids are decomposed by the action of thiosulphate into silver and halogen silver, which after being converted into silver thiosulphate, dissolves as a double salt. The place of the α silver subhaloid germ and the β silver subhaloid is consequently taken by silver, which also possesses the property of germination, as appears from the development of primarily fixed plates. Strong solarization, however, still produces solarization during development after primary fixation, so that the reaction between β silver subhaloid and the thiosulphate in the binding material is a slow one, as is the oxidation process already referred to. So if a highly sensitive course grain plate, i. e. one with a small grain surface, in other words, with a small quantity of β silver subhaloid, which has been exposed till solarization has set in, is treated, the reaction in the gelatine will be complete sooner than with a greater quantity of β silver subhaloid in the same gelatine plate, as is the case with fine grain emulsions. The reducibleness will consequently show an increase (not to be confounded with acceleration), so that in proportion to the strength of the thiosulphate solution employed, and the duration of the action, the solarization will be removed, either to a smaller or to a greater extent, or totally.

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[1]) Phot. Korresp. 1901; S. 350.

LÜPPO-CRAMER. Wissensch. Arbeiten. 1902; S. 41.

LÜPPO-CRAMER. Phot. Probleme 1907; S. 146.

This phenomenon was observed experimentally by KOGELMAN [1]), VIDAL [2]) and E. ENGLISCH [3]), while LÜPPO CRAMER [4]) could not demonstrate solarization at all with primarily fixed, highly sensitive, coarse-grain plates, which fix more slowly than fine-grain ones.

Sulphocyanides act analogously in reducing solarization.

In the case of SABATIER's polarization the strong decrease (disappearance?) of development of the image after it has appeared is not to be ascribed to the decrease of the number of germs, as they have already fulfilled their function [5]). So the decrease of development can only be a reduction of the speed of development, which is to be accounted for by a strong decrease in the supply of feeding substance. From the theory given above of the so-called chemical method of development it has appeared that the silver subhaloid proves to be less soluble in the developer than the silver haloid. Therefore the more soluble silver haloid can, after reduction, be precipitated upon the germ, which still remains unchanged in its place. Consequently if the secondary exposure is of an intense nature, the feeding substance will be enveloped by subhaloid, by which development is retarded. This will take place in the developer all the more readily, because it is an absorbent of halogen.

In conclusion reference may be made to a possible explanation of the variations in the optical sensitizing of the photographic plate which is characterized by a considerable decrease in reducibleness being noticeable in the places where the power of absorption is spectrally highest. From M. ANDRESEN's experiments [1]) it appears that the photo-chemical decomposition products remain in contact with the dyestuff, so that the *α* silver subhaloid obtains a different colour sensitiveness. In this case complications may occur, if the dye is at the same time an absorbent of halogen (a chemical sensitizer), by which it changes or loses its absorption spectrum, and a consequent promotion of the photo-chemical decomposition action sets in.

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[1]) J. M. EDER. Jahrb. f. Phot. u. Repr. 1895; S. 419.

[2]) Bull. Soc. franç. Phot. 1898; p. 583.

[3]) J. M. EDER. Jahrb. f. Phot. u. Repr. 1901; S. 608.
. . . . . . 1902: S. 79.
. . . . . . 1904; S. 423.

[4]) LÜPPO-CRAMER. Phot. Probleme. 1907; S. 150.

[5]) So far there is not a single reason for assuming that this reduced substance consists exclusively of α silver subhaloid germs, which pass into β silver subhaloid by the secondary exposure, by which further development would be checked.

VI. *Conclusions.*

From what has been said a few conclusions may be drawn, which may be of importance in practice.

Both *α* silver subbromide and iodide are substances of a much greater sensitiveness to light than the corresponding silver haloid.

Consequently if it was possible to compose emulsions in which these substances were present side by side with the silver haloid which as feeding substance is indispensable for development, plates would be obtained not only of a higher sensitiveness than the present ones, but in them a chemical sensitizer would be practically desirable in every respect to prevent regression. Such plates would entirely comply with the reciprocity rule, and would render the light gradations of the objects to be photographed much more correctly, which may be of great value to astronomical photography, e.g. for the determination of the light intensity of stars by the photo-chemical method (Photometry).

The *α* silver subhaloid can be optically sensitized, so that its application might obtain a great extension. The exact colour sensitiveness of the *α* silver subhaloid separately is not yet known exactly. (That in the case of secondary exposure the highest sensitiveness is situated in the red, the lowest in the green, points with great probability to the *α* silver subhaloid being a green substance). The experiments mentioned indicate everywhere only the difference in light sensitiveness between silver haloid and the *α* silver subhaloid. The greater this difference, the more favourable the result obtained. Consequently the best expectations might be entertained with respect to silver chloride plates with *α* silver subiodide, and it is an open question whether the latter may not be allowed to ripen too. The *β*-silver subhaloid seems to possess, photo-chemically, an extremely low sensitiveness, which can only be advantageous in practice.

This process yields directly polarized copies (positives through the camera). On one hand this seems an objection, as all printing methods are based upon the production of normal copies (the negative process). But it should be borne in mind that hitherto very few researches have been made in this domain.

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[1]) Phot. Korresp. 1898; S. 504.

For direct colour photography [1]) with colour elements lying side by side under the emulsion, according to L. Ducos du Hauron's system (which especially lately has given promise of a great future), which requires directly polarized copies, and which so far has only succeeded in obtaining them in an indirect way, this method would also be practically valuable.

In this direction little experimenting has hitherto been done from a photo-chemical point of view, and even in what has been done it has been impossible to account for the phenomena that occurred, so that for the present there is no need for us to take too pessimistic a standpoint with reference to this.

VII. *The shape of the image in the case of Herschel's effect.*

As to the shape of the image in the case of Herschel's effect fig. 8 may be referred to.

It is clear that after the critical exposure the normal copy is again a surface image. If a considerable portion of the surface silver haloid present has already been decomposed into *a* silver subhaloid and halogen, the secondary exposure will not be able again to form as much *a* silver subhaloid as would have been the case if the primary exposure had not taken place. A negative is obtained then the density of which is less than that of a plate not previously exposed. This case presents itself in the sky *a* in fig. 5.

Advanced primary exposure may result in solarization, in which case the surface silver haloid can no longer supply the same quantity of germs as was present before: Herschel's effect then coalesces with solarisation, and the critical exposure can no longer be ascertained.

The greater light sensitiveness of the *a* silver subhaloid as compared with that of silver haloid is also shown in the amount of halation. In fig. 5 the foliage of the tree is affected by it, while the houses round the sky near *a* do not show any; there the halation was too slight to exceed the liminal value of the silver haloid. In fig. 6 the dark lead frame of the window also shows the destruction of the germ owing to halation; on the other hand on the right side it was able to form fresh germs through a more powerful action.

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[1]) I expressly call this method "direct", because I cannot agree to the judgment of a number of others, who want to classify it among the indirect methods. They say that it is not direct colour photography, but three-colour photography, ignoring the fact that the bleaching method which is reckoned to belong to the direct methods, is also three-colour photography. Nor can I agree to A. v. Hübl's classification (Phot. Rundschau, 1908, p. 2), by which the bleaching process would be assigned to the indirect methods. The fact of the matter is that the difference is only a question of method, i.e. whether the colours are obtained directly after exposure (with development), or only through subsequent addition.

That the difference in light sensitiveness between the germ and the silver haloid is great, appears from the backs of the dogs, and from the shoulders of the female figure to the right in fig. 5. The narrow white strip indicates that after the germs had been totally destroyed at the free surface, for some time longer the silver haloid again began to supply germs, first in the most strongly exposed portions, and then gradually also in those which received less exposure. Consequently if the action of the light increases, these strips must become narrower, which is also shown by the figure, as the dog to the left was more glossy than the one to the right.

The white strips along the edges of the black objects in the background are of quite a different nature. These are to be ascribed entirely to irradiation, for in the case of stronger light intensities occurring side by side they are broader than where the intensity is less great.

If observed very closely by light reflected at an angle, these bright strips are seen to possess a greater gloss than the portions immediately adjoining them. To the left of the tree top this is easier to see than to the right. The light from the wall has acted more intensely to the left than to the right, and notwithstanding the polarization a copy of greater density is shown there. That the critical exposure should have been surpassed, is out of the question here.

This phenomenon, too, can be accounted for according to the theory given, for in this theory it has been stated, that the critical exposure is not surpassed till the secondary exposure has formed a greater amount of *a* silver subhaloid than is present in consequence of the primary exposure. Consequently after the liminal value of the silver haloid has been surpassed, a new surface image can originate, the density can increase afresh, and still at the same time the copy will remain polarized.

All the abnormalities in the figures 5 and 6 have thus been accounted for.

In conclusion I wish to express my best thanks to Mr. P. H. Eykman for finding materials and placing them at my disposal, and for his constant interest in my work.

Physics. — "*Isotherms of diatomic gases and their binary mixtures. VIII. The breaking stress of glass and the use of glass tubes in measurements under high pressure at ordinary and low temperatures*". By Dr. H. Kamerlingh Onnes and Dr. C. Braak. (Communication n°. 106 from the Physical Laboratory at Leiden by Dr. H. Kamerlingh Onnes).

(Communicated in the meeting of April 24, 1908).

§ 1. *Introduction.* With former determinations of isotherms (Comms. n^{os}. 78 April 1902, 97^a March 1907, 99^a Sept. 1907, 100^a and 100^b Dec. 1907, 102^a Dec. 1907 and 102^b Febr. 1908) we could not raise the pressure above 60 atm. For in order to reach the required accuracy of about $^1/_{2000}$ we want a manometer which is reliable to the same degree. And till now we could only reach this degree of accuracy by means of a calibration with the open manometer described in Comm. n°. 44 (Nov. 1898) which reads to 60 atm. only. Already long ago we intended to include the higher pressures in our investigation. As a first step in that direction we have raised the upper limit of the pressure to 120 atmospheres. For while keeping the same arrangement we could easily complete the existing open manometer to one of the same accuracy reading to 120 atmospheres by merely adding a number of new manometer tubes of greater resisting power than those we had.

The new manometer and also the other apparatus intended for pressures to 120 atmospheres are nearly completed and will soon enable us to determine the isotherms to 120 atm. Afterwards we hope that these will be followed by measurements at still higher pressures. It seems even possible to reach 500 atmospheres with almost the same accuracy.

For all these investigations it is a great advantage when the piezometer- and barometer tubes can be made of glass. Therefore we have investigated in how far this would be possible with regard to the breaking stress of glass.

The breaking stress of glass has been investigated most at ordinary temperature, because it is in the first place desirable that the reservoirs of the manometer tubes of the open manometer and the divided stems of the piezometer tubes should be made of glass.

To these measurements we have added a series of determinations at lower temperatures in order to judge to what extent glass piezometer reservoirs could be used for the higher pressures at these temperatures.

Investigations on the maximum strain of glass have been made by **Galitzin**[1]) and by **Winkelmann** and **Schott**[2]). The former has determined the inner pressure which cylindrical glass tubes can resist, the latter two have determined the maximum strain of glass rods. **Galitzin**'s determinations, however, were made only at relatively small pressures, those of **Winkelmann** and **Schott** only at ordinary temperature.

In our investigation we partly follow the method of **Galitzin**. From the theory of elasticity we can derive in connection with the dimensions of the apparatus the maximum tension in the glass from the maximum pressure which the glass tube resists. The results obtained in this way were compared with the direct data obtained in a second series of measurements, where the maximum strain of glass rods was determined. If we take into consideration the material investigated, it is not astonishing that the results of the two series show irregular differences. These differences however are of no influence upon some general conclusions that may be drawn from the measurements.

§ 2. *Determinations at ordinary temperature.*

Survey of the observations and arrangement of the measuring apparatus.

1. *Determination of the maximum inner pressure.*

The experiments were made with ordinary Thüringer glass. A cylindrical reservoir of the glass to be investigated was fused on to a thick walled glass capillary. The capillary was provided at its end with a steel nut with a hexagonal part by means of which it could be screwed on to a steel capillary which is connected to a pressure pump with a metal manometer. For measurements to 200 atms. it was fixed on the glass by means of sealing wax, for higher pressures it was soldered to the glass (comp. Comm. N°. 99^a § 15, October 1907). If carefully made this connection proved able to resist the highest pressures (1200 atms.) The tubes were previously annealed carefully.

According to their dimensions they can be divided into three kinds:

a. thick-walled tubes with large inner bore.

b. thick-walled capillaries.

c. thin-walled tubes with large inner bore.

It will appear that these three kinds of tubes give results different for each group.

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[1]) Bull. de l'Acad. Imp. des Sciences de St. Pétersbourg, V^e Serie, B. XVI N^o. 1.

[2]) Wied. Ann. 51.

The accuracy of the manometer is about 2 $^0/_0$, which is quite sufficient for our purpose.

2. *Direct measurement of the maximum strain T_m by the determination of the breaking stress.*

In order to prevent as much as possible unequal strain during the suspension we have used here glass threads of at the most 0.6 mm. thickness [1]).

In order to reduce the tensions to minimum the glassrod was bent to a hook at either end. It was then suspended by the upper hook and the rod was drawn out in the middle to a thread by applying a certain force to the lower hook in about the same way as in the actual experiment. The weight used was a beaker into which water flowed.

§ 3. *Results.*

1. *Determinations with cylindrical tubes and internal pressure.*

In order to facilitate a comparison with Galitzin's results we take the same value $\frac{1}{4}$ for the coefficient of contraction. Let P_m be the maximum internal pressure, $2R$ the external diameter, $2R'$ the inner diameter (this is further on expressed in mm), and let $n = \frac{R}{R'}$, then we can represent the maximum tension T_m in the glass, (in this case that of the internal portions of the glass in a direction perpendicular to the axis of the cylinder) by:

$$T_m = \frac{1}{4}\left\{5P_m + 7\left(\frac{P_m-1}{n^2-1} - 1\right)\right\}.$$

If, as is the case in the following tables, P_m is expressed in atmospheres, we find T_m expressed in KG/mm^2 (as it is given in the following tables) by multiplying the value found above by 0.01033.

For the three series mentioned in § 2 sub a, b and c the results have been combined in the table below. The meaning of the columns will be clear after what has just been said. Where several results are given under one number we have after the tube had partly burst (for instance so that only the end had broken off, or the tube had broken near the steel piece) used the same tube again for the following experiment.

The results for T_m are lowest for series a and highest for series b. In the last series this is especially the case for the tubes with a very

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[1]) In the experiments of Winkelmann and Schott where thicker rods of 10—20 mM^2. section were used this required great care.

TABLE I. Maximum internal pressure and tension of cylindrical glass tubes.

No.	$2R$	$2R'$	n	P_m	T_m
Series *a*					
1	9.3	3.5	2.66	340	5.38
2	8.8	4.0	2,20	280	4.91
3	8.7	4.2	2.07	230	4.21
4	9.4	3.2	2.94	270	4.10
5	9.2	3.0	3.07	380	5.70
6	9.7	4.2	2.31	370	6.30
7	10.4	4.0	2.60	240	3.83
8	12.8	5.8	2.21	260	4.54
9	17.6	5.0	3.52	290	4.19
Series *b*					
10	7.4	1.00	7.40	510	6.74
11	6.8	1.00	6.80	420	5.57
12	7.5	0.27	27.78	460	5.93
13	6.5	0,35	18.57	500	6.46
14	6.7	0.24	27.92	540 800 1100	6.97 10.33 14.21
15	6.7	1.08	6.20	530	7.08
16	5.9	0.70	8.43	680	8.94
17	5.8	0.46	12.61	1200	15.61
18	5.9	0.62	9.52	820	10.74
19	5.3	0.46	11.52	920	11.99
20	5.5	0.46	11.96	1060	13.80
21	6.6	1.00	6.60	660	8.78
22	7.2	1.40	5.14	520	7.07
23	6.4	1.35	4.74	520	7.13
Series *c*					
24	3.8	2.42	1.57	283	7.12
25	5.6	4.00	1.40	193	6.09
26	6.4	4.78	1.34	221	7.84
27	6.9	3.91	1.76	329	7.06
28	7.4	5.11	1.45	179	5.21
29	7.9	5.46	1.45	157	4.57
30	3.5	2.26	1.54	261	6.78
31	6.8	5.13	1.32	203	7.52
32	7.4	5.19	1.43	201	6.04
33	6.8	5.78	1.18	66	3.83
34	3.8	2.42	1.57	377	9.49
35	3.8	2.50	1.52	277	7.36
36	6.0	4.37	1.37	179	5.96
37	6.8	5.17	1.31	159	6.02
38	6.8	4.85	1.40	169	5.33
39	7.3	5.62	1.30	109	4.22
40	7.8	7.31	1.067	54	7.60

small inner bore if we except nos. 12 and 13 where the soldering was ineffective. Helped by the experience made we have treated the following tubes more carefully. With the tubes which have burst under a too low pressure the existence of irregular tensions appears clearly from the way of bursting, where the break has a transverse or irregular direction and not, as theory requires, parallel to the axis.

2. *Maximum strain of glass threads.*

The diameter of the threads lies between 0.1 and 0.6 mm. The results are combined in the two following tables. The bore was determined by a measurement of the diameter in two directions at right angles. The mean of these two measurements is given in the tables. The first table contains the results obtained with glass threads which have undergone only the operation mentioned sub § 2. To investigate the influence of irregularities which thus may remain in the structure of the glass we have made a series of measurements by means of threads which had beforehand been heated to incandescence and then cooled very slowly. The results of this series are combined in table III.

TABLE II. Maximum strain of uncooled glass threads.

Stress in grams	Diameter in mm	T_m in KG/mm^2	Stress in grams	Diameter in mm.	T_m in KG/mm^2
257.6	0.119	23.1	2615	0.424	18.4
496.5	0.192	17.5	2785	0.446	17.8
457.8	0.159	22.9	1425	0.351	14.7
2325	0.384	19.8	1635	0.370	17.5
1175	0.257	22.7	1325	0.325	16.0
1475	0.325	17.6	1555	0.298	22.4
1695	0.311	22.4	2335	0.370	21.5
4105	0.487	22.1			

Except the thread for which T_m is lowest viz. 14.7 all the threads of table II show where broken a sharply ridged structure while we find at the edge a small semicircular smooth spot as was found by **Winkelmann** and **Schott**[1]).

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[1]) p. 718 loc. cit.

TABLE III. Maximum strain of cooled glass threads.

Stress in grams	Diameter in m.m.	T_m in $KG./mm^2$	Stress in grams	Diameter in m.m.	T_m in $KG./mm^2$
2920	0.438	19.4	1910	0.325	23.4
3530	0.597	12.6	1760	0.322	21.6
2120	0.532	9.5	2850	0.445	18.3

With regard to the series of table III we may remark the following. In order to prevent changes of form of the threads suspended in the furnace and softened by the heat under the influence of gravitation, which afterwards during the measurements might give rise to irregular tensions, we have shaped the extremities (cf. § 2) not into hooks as in the former series but to closed rings in such a way that the whole becomes as symmetrical as possible with regard to a plane through the longitudinal axis. A comparison of the tables II and III shows that the two methods lead to the same results.

Of the glass thread with the lowest T_m (cf. table III) the section was little ridged but smooth, to the next value of T_m ($= 12.6$) belonged a relatively large smooth semicircular spot, while for the highest T_m ($= 23.4$) no spot was to be seen, but the whole section showed a very sharply ridged structure. All these facts agree with what has been found by WINKELMANN and SCHOTT [2]).

On the plate we show the structure of the sections of a couple of threads at the place where the thread has broken. They both clearly show the smooth parts and the structure radiating thence. The smallest diameter of the sections is 0.530 and 0.555 mm. respectively.

§ 4. *Conclusions.*

Table I shows that as to the series *a* and *c* our results agree tolerably well with those of GALITZIN [1]).

Those of the series *b*, however, show that the result derived by him for the maximum internal pressure, viz. 623 atms. is too low, because the highest pressure observed by us is 1200 atms. For the tubes of the series *b* T_m appears to lie higher than would be expected from the observations in the two other series. Probably this must be explained as follows. From a comparison between the 3 series it appears that series *a* gives the lowest results for T_m, series *b* the highest. The fact that the values for *a* are lower than for *c*, must probably be ascribed to the circumstance that with almost equal internal bores the wall is thickest for the first series and hence the chance of abnormal stresses is greater. For series *b* the wall is thicker than for *c*, but the inner bore is much smaller, and hence the existence of inequalities and scratches on the surface which unfavourably influence the breaking stress [1]) are reduced to a minimum. For the tubes for which $2R' = 1$ mm. it seems that the two factors neutralize each other, for those with the smaller inner bore the favourable influence of the surface being smaller preponderates.

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[1]) loc. cit.

[2]) Table I p. 12 and 13, loc. cit.

In order to investigate in detail in how far the above mentioned two unfavourable factors influence T_m we have applied the direct determination with thin glass threads of which the surface is as smooth as possible and where owing to the small bore abnormal tensions are necessarily small. The results which are much higher than those of WINKELMANN and SCHOTT, agree with those found by means of the first method and seem to justify the supposition made above about the unfavourable influence of a not perfectly smooth surface and inner abnormal stresses. They point to an upper limit for $P_m = 1700$ atms.

§ 5. *Determinations at low temperatures.*

The determinations in liquid air were made in the same way as those at ordinary temperature. The lower hook of the glass thread was fastened to a wooden bearer, placed beside the thread in a vacuum glass with liquid air. The first determinations gave results which differed much from the later ones. Their mutual agreement is very bad and they are characterized by very high values for the maximum strain, which vary from 44 to 73 KG. per mm.^{2} while for the ordinary temperature the highest strain was 23 KG. per mm.^{2}. Also the structure of the section was totally different, being scarcely ridged but smooth. The smooth spot on the section was as a rule missing. In these measurements the threads were pulled asunder almost immediately after they had been placed in liquid air. Before the following measurements they were left at least 20 minutes in the bath of low temperatures. The latter gave lower results with a better mutual agreement. The structure of the section is similar to that at ordinary temperature, generally a little less distinct. The results are combined in the following table.

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[1]) Cf. WINKELMANN and SCHOTT, loc. cit.

Dr. H. KAMERLINGH ONNES and Dr. C. BRAAK. Isotherms of diatomic gases and their binary mixtures. VIII. The breaking stress of glass and the use of glass tubes in measurements under high pressure at ordinary and low temperatures."

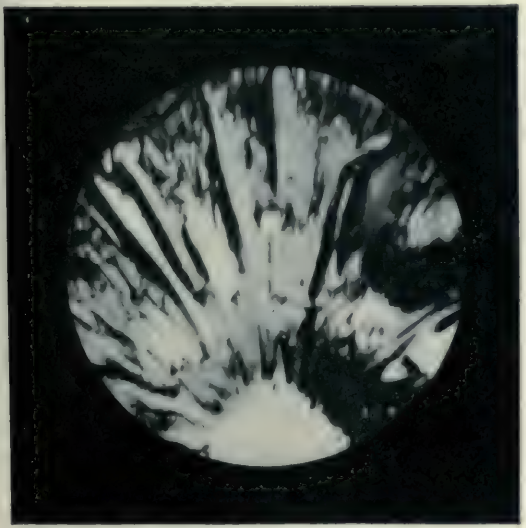

Fig. 1.

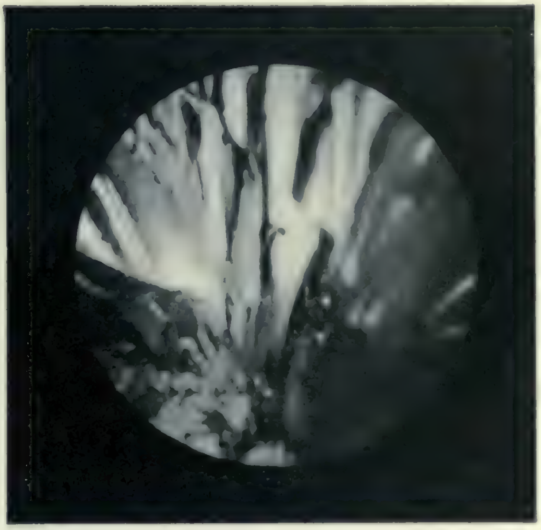

Fig. 2.

TABLE IV. Maximum strain of glass threads at the temperature of liquid air.

Stress in grams.	Diameter in mm.	T_m in KG/mm^2	Stress in grams.	Diameter in mm.	T_m in KG/mm^2
1993	0.280	32.4	2498	0.297	35.9
2653	0.372	24.3	2055	0.286	31.9
2523	0.290	38.2	3550	0.359	35.1
1293	0.236	29.5	3865	0.396	31.3

The results are still much higher than for the ordinary temperature, a very favourable result for measurements at low temperature.

Lastly a single determination in liquid hydrogen was made. Fifteen minutes after the thread had adopted the temperature of the bath it was pulled asunder. The total weight was 3013 grams, the diameter 0.271 m.m., hence the maximum strain in $^{KG}/_{mm^2} = 52.1$ again much higher than at the temperature of liquid air. The structure of the section was striated, unridged and no smooth part occurred.

Zoology. — "*Poterion a Boring Sponge.*" By Prof. G. C. J. Vosmaer.

(Communicated in the meeting of May 30, 1908).

In 1822 Hardwicke published [1] a short notice on a remarkable "Zoophyte, commonly found about the Coasts of Singapore Island." The author stated that it belonged to the Sponges, and called it *Spongia patera*. Evidently not acquainted with this publication Schlegel 1858 [2] proposed the name *Poterion neptuni* for a sponge, which universally is considered to be identical with Hardwicke's sponge. According to the rules of nomenclature the object has, consequently, to be called *Poterion patera* (Hardw.), as first pointed out by Sollas [3]).

Both Hardwicke and Schlegel state that the sponge is fairly common. No wonder that this object, which presents itself as a gigantic cup, with a height of more than 1 M. and an aperture of 30 cm. or more, drew the attention of sailors. It is also found in many museums, especially in Holland. The Leyden Museum of Natural History, the Museum of the Utrecht University and the Museum of the Amsterdam Zoological Gardens ("Artis") possess beautiful specimens, together more than 30. This rich material induced Hartinc

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1) Asiatic Researches XIV, p. 180.

2) Handleid. Dierkunde II, p. 542.

3) Ann. en Mag. Nat. Hist. (5) VI, p. 441 (1880).

to study the sponge, as far as the dry specimens allowed it. Harting published in 1870 his well-known "Mémoire sur le Genre Potérion",1) the result of an examination of 27 specimens. Since that time the sponge has hardly been mentioned. It seems indeed strange that since Schlegel's publication — half a century ago — these gigantic specimens which obviously were far from rare were never or hardly ever sent to any of our museums, and that none of the numerous expeditions of later times brought home even a single specimen of *Poterion.* As far as I can judge even the Siboga-expedition is no exception. My request to several people in our colonies in the Malay Archipelago remained unanswered, till last year, when I received a letter from Dr. P. N. van Kampen, assistant Zool. Mus. Buitenzorg, mentioning, that in his presence three specimens of *Poterion* were dredged off Bantam at a depth of about 25 M. Thus the sponge was found again at last. Dr. van Kampen was kind enough to send me fragments, well preserved in 96°/$_0$ alcohol; he also told me from time to time when new specimens were collected all from the West part of the Java-sea. We learn from this, that the sponge is not rare.

Since nothing was known about the anatomy of the "soft parts" of *Poterion,* I was rather anxious to study microscopical sections of well-preserved specimens. It struck me at once that the structure of this *Poterion* closely resembles that of the so-called *Osculina polystomella O. S.* of which I prepared a description and drawings many years ago2).

Now this *Osculina* is nothing but the "free form" of a boring sponge, as first pointed out by Carter3); Lendenfeld afterwards (1895)4) proclaimed *O. polystomella* as the free form of *Vioa viridis O.S.* Independently of Lendenfeld I arrived at about the same result.

It was, therefore, but a logical conclusion to suppose that *Poterion patera* was likewise the free stage of a boring sponge, and I begged Dr. van Kampen to look whether in the localities where *Poterion* was dredged, shells, corals, limestone or similar substances occurred which were attacked by Clionidae. Meanwhile I reexamined the specimens of *Poterion* in the Leyden Museum. The director of the Museum, Dr. F. A. Jentink was so kind as to allow me to cut

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1) Natuurk. Verhandel. Prov. Utr. Gen.

2) MS. for Fauna and Flora of the Bay of Naples. By unforeseen events the publication had to be postponed more than once. I am indeed very glad to be able to say that the bulk of the MS. is ready and I hope that no serious interruptions will prevent me from going to press soon.

3) Ann. d. Mag. Nat. Hist. (4) V.

4) Zool. Anzeig. p. 160.

one specimen across for further examination. This I did with a specimen to which I gave the number 338. At the base of the sponge, which is somewhat broadened, I found between the "roots" much sand, rather large pebbles and a number of shells. One of these is a *Voluta scapha* Gmel. of about 10 cm. × 5 cm.; it shows on its surface numerous holes of a boring sponge, which has pierced the shell a good deal and which has already destroyed a portion of the surface. Microscopical examination of the dried sponge-substance in the interior of the *Voluta* proved that the spiculation closely resembles that of the *Poterion* 338. The sponge substance on the surface of the shell is continuous with that of the *Poterion*. My supposition that *Poterion* represents the free stage of a boring sponge is hereby proved. I am not yet prepared to say whether it is identical with one of the numerous known species. I hope to be able to settle this later on and to give a full account (with illustrations) of the subject. I shall then discuss why only a small portion of *Voluta* is destroyed and the possible mode of growth. As to the anatomy of the spirit-specimens now at my disposal, a brief account may follow here.

A longitudinal section through the wall of the cup, somewhat nearer its basis than its border, where the wall has a thickness of about 25 mm., shows that the cortex has on both sides about the same thickness, viz. 1—5 mm. The parenchyma shows large incurrent and excurrent canals, both surrounded by a transparent tissue. The main incurrent canals have a diameter of 0.5 mm., the main excurrent canals of 0.5—1 mm.; with the transparent tissue the former are, on an average, 3 mm. the latter 5 mm. Both enter deeply into the parenchyma; the former 15—20 mm., the latter 10—15 mm. In their course through the parenchyma the incurrent canals show several round apertures — the beginnings of secondary canals. The mass between these main canals and the surrounding tissue is composed of a crumb-of-bread like substance, and the trabecular network of the skeleton. At this part of the cup the incurrent apertures, stomions, are situated on the outside. They are congregated into pore-areas of indistinct outline; these areas are nevertheless clearly visible as dark brownish spots on a buff-coloured background. The areas have a diameter of a little more than a millimeter, and are situated at about the same distance from each other. In some places the areas are somewhat sunken; in dry specimens this shrinkage goes a good deal farther. I have not been able to detect the stomions on the surface; but sections clearly show that they are placed more or less in rows which start from a common centre. They are the apertures of narrow and short canals which open just under the dermis into wider canals of which generally 5—6 unite in a common centre. These canals cause the star-like figures, already described by Harting. Tangential sections show this plainly; it becomes then obvious that these cortical canals sometimes ramify; but the final result is always that on an average five unite into a common wider canal, at right angles to the surface which runs through the rest of the cortex. It is evident that this latter canal corresponds to the incurrent chone [1] of Tetraxonia, as sections at right angles to the surface prove.

The incurrent chones lead into the main incurrent canals; some of these, as stated above, run more or less straight on for about 15—20 mm. at right angles to the sponge surface; they then bend and run in a direction almost parallel to the sponge-surface. In their course they give off branches, which ramify and terminate between a group of the mastichorions. These are ellipsoidal in shape and open with wide apopyle into the excurrent canals, the system being eurypylous. A certain number of excurrent canals flow together and finally open into the main canals, mentioned above; they traverse the cortex with excurrent chones, which open by procts on the inner surface of the cup.

The soft tissue, surrounding the main canals, excurrent as well as incurrent, is very remarkable. I found the same sort of tissue in many sponges, but especially well developed in the so-called *Osculina polystomella*. Lendenfeld has seen this tissue, and in his description of "*Papillella suberea*" says [2]: "Das hyaline Gewebe, welches die Hauptkanäle umgiebt . . . . besteht aus einer glashellen Grundsubstanz, in welcher zahlreiche multipolare und auch bipolare Zellen liegen, deren lange und schlanke, verzweigte Ausläufer überall mit einander anostomosiren, so dass hier ein engmasschiges, spongiöses Netz zu Stande kommt. In einigen der Knotenpunkte dieses Fadennetzes liegen die Zellleiber mit ihrem kugligen Kern, in anderen trifft man nur unbedeutende Plasmaanhäufungen an." In my MS. description of this tissue in Clionidae I differ somewhat from LENDENFELD's interpretation; in *Poterion* I find the same sort of tissue, only still more pronounced. The fact is that the reticulum is by no means simply formed by a network of "Ausläufer" of cells, as it becomes clear by careful focussing that a number of the supposed thread-like processus are really membranes. In *Poterion* these membranes are sometimes of enormous size, even larger than in *Cliona* (*Osculina*). The tissue has a close resemblance to the so-called lymphoid or reticular tissue, as RANVIER and PEKELHARING conceive it.

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[1] Of course I use here the term chone in the sense of Sollas, and not in the sense of Lendenfeld. This latter author is entirely wrong in using chone as a synonym for sphincter. Sollas wrote in 1880 (Ann. & Mag. Nat. Hist. (5) v. p. 135): "The cortex is traversed by the intermaginal cavities of Bowerbank, or, as I shall term them, the "cortical funnels" or "chonae". They consist essentially of a tube divided by a sphincter into a shorter proximal and a longer distal part, the "ectochone" and "endochone" respectively". Apart from the evident lapsus that in this sentence the words ecto- and endochone stand in the wrong place Sollas's meaning is plain enough and this definition is generally accepted. However Lendenfeld has another opinion. Thus, for instance, he writes in 1897 (Die Clavulina der Adria, p. 102—103): "In halber Höhe der Rinde . . . . . vereinigen sich diese Sammelkanäle zu vertikalen Stammkanälen . . . . ." And further: "Oben ganz dünn, verdickt sich diese schlauchförmige Einfassung des Stammkanales . . . . . nach unten hin sehr beträchtlich und bildet proximal, in der Umgebung der erwähnten Verengung, mächtig verdickt einen starken Sphincter, der als eine Chone aufzufassen ist". I do not wish to discuss the matter here at length. The quoted passages leave no room for misunderstanding.

[2] Clavulina der Adria p. 104—105.

As to the skeleton of *Poterion*, this is formed by a trabecular very firm network of bundles of closely packed tylostyles. I found in *Osculina* that in some portions of the skeleton the spicula were united by a little spongin. The same holds true for *Poterion*. This is, however, only the case in the centre of the pillars or trabeculae; there is a mantle of spicules at the periphery which is devoid of spongin. The spicula of *Poterion* are tylostyles; the spicule for which I proposed[1]) the name spinispira I did not find in the specimens of *Poterion* I examined. We know, however, that in the genus *Cliona* itself spinispirae are often very rare or absent, especially in the so-called free stage. I am of opinion that *Papillina suberea O.S.* is identical not only with *Osculina polystomella O.S.*, but also with *Papillina nigricans O.S.* and *Vioa viridis O.S.* They are all nothing but modifications of the very variable *Cliona celata*, as I hope to prove in my "Sponges of Naples". LENDENFELD (1897 l.c. p. 99) considers *Papillina suberea O.S.* as a species different from *Papillina nigricans O.S.* This is especially on account of the absence of spinispirae in the former, in a type-specimen of which LENDENFELD failed to find them. I found, however, in the collection of the Zoological Station at Naples a sponge labelled by SCHMIDT *P. suberea*; in *this* specimen I did find spinispirae. I found them likewise in some of the specimens I collected near Trieste. For these reasons I cannot distinguish *nigricans* from *suberea*. Consequently there is in the absence of spinispirae in *Poterion* no ground for not placing this sponge in the same group as *Cliona*, since in every respect the anatomical structure of *Poterion* resembles that of *Osculina*.

Leyden, May 14, 1908.

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[1]) On the shape of some Siliceous Spicules of Sponges. (Kon. Akad. v. Wetensch. Amsterdam, 1902. Proceedings p. 104—114).

Chemistry. — "*Reduction of aromatic nitro-compounds by sodium disulphide.*" By Dr. J J. Blanksma, (Communicated by Prof. A. F. Holleman).

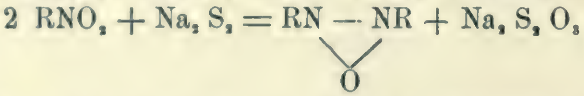
(Communicated in the meeting of May 30, 1908).

I have pointed out previously [1]) that sodium disulphide may act on aromatic nitro-compounds in two different ways, namely by substitution or by reduction.

1. Substitution occurs when halogen atoms or nitro-groups are present which under the influence of *ortho*- or *para*-placed nitro-groups have become moveable. These on being treated with sodium disulphide are readily replaced by S_2 and the disulphides thus formed may be converted by oxidation into sulphonic acids. A fairly large number of these cases have been communicated previously [1]).

2. Reduction takes place when the nitro-compounds do not contain any moveable halogen atoms or nitro-groups; a nitro-group is then reduced to an amido-group, whilst generally a small quantity of azo-oxycompound is also produced according to the equations:

$$RNO_2 + Na_2S_2 + H_2O = RNH_2 + Na_2S_2O_3$$



$$2\ RNO_2 + Na_2S_2 = \underset{\diagdown\,O\,\diagup}{RN - NR} + Na_2S_2O_3$$

A preliminary investigation had shown me previously that alcoholic solutions of nitrobenzene and *o*-nitrotoluene are readily converted by Na_2S_2 into aniline and *o*-toluidine, the Na_2S_2 being oxidised to $Na_2S_2O_3$. *m*-Dinitrobenzene and *p*-dinitrobenzene when treated with Na_2S_2 yielded, respectively, *m*-dinitroazo-oxybenzene and *p*-dinitroazobenzene. It was then [2]) our intention to further investigate the reducing action of Na_2S_2.

Meanwhile, however, a patent has been granted to Kunz [3]) for the reduction of aromatic nitro-derivatives to amido-derivatives by means of sodium disulphide in aqueous solution and afterwards sodium disulphide has been used by Brand [4]) as a partial reducing agent.

I have now studied the reduction of aromatic nitro-compounds by Na_2S_2 in alcoholic solution in a number of cases. The reduction is carried out as follows:

Six grams of nitrobenzene are added to a boiling solution of 12 grams of crystallised sodium sulphide and 1.6 gram of sulphur in

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[1]) Dissertation. Amsterdam 1900; Rec. 21. 121, 141.

[2]) These Proc. 1900, (Oct.)

[3]) Chem. Centr. 1903 II 818.

[4]) Journ. f. pract Chem. 1906. (2) 74, 499.

300 cc. of 96 °/₀ alcohol. After boiling for 6 hours, the alcohol is recovered by distillation and the aniline which still contains a little nitrobenzene is distilled in a current of steam. It is then converted into the hydrochloride to separate it from the admixed nitrobenzene; about 5 grams of aniline hydrochloride are obtained. In the same manner were treated *o-m-* and *p*-nitroanisol, *m*-chloro- and bromonitrobenzene and dichloro- and dibromonitrobenzene 1. 3. 5. from which were readily obtained the corresponding amido-derivatives to the extent of about 70 °/₀ of the theoretical quantity.

In the case of *ortho-* and *para*-chloronitrobenzene where the halogen atom is replaced by S_2 a simultaneous reduction takes place to a slight extent with formation of *o-* and *p*-chloroaniline.

Ortho- and *m*-nitrotoluene readily yield *ortho*-and *meta*-toluidine; with *para*-nitrotoluene a secondary reaction occurs, *p*-amidobenzaldehyde being formed as well as *p*-toluidine [1]).

Besides the above mentioned mononitro-compounds a few dinitro-compounds were subjected to a partial reduction. From sym-dinitrotoluene we readily obtain by means of alcoholic Na_2S_2 3-nitro-5-amidotoluene; sym-dinitroanisol yields 3-nitro-5-amidoanisol; from 2-4-dinitroanisol (or phenetol) is obtained 2-amido-4-nitroanisol (or phenetol) whilst sym. trinitrobenzene yields 3-5-dinitraniline. A small quantity of the azo-oxycompounds is generally formed in addition to the amido-derivatives. I will also point out that in the reducion with Na_2S_2 the formation of chlorinated byproducts, which are often generated in the reduction of aromatic nitro-compound with Sn and HCl, is avoided. The fact that sodium disulphide may be weighed also gives it an advantage over ammonium sulphide as a reducing agent.

From the above facts it is obvious that an alcoholic solution of Na_2S_2 may be used as a convenient reducing agent.

Physiology. — "*About the determination of hardness in muscles.*" By A. K. M. Noyons, Assistant in the Physiological Laboratory at Utrecht. (Communicated by Prof. H. Zwaardemaker.)

(Communicated in the meeting of May 30, 1908).

At an inquiry into the causes and qualities of the autotonus it struck me how a muscle seemed to become harder, as its autotonus increased. Hitherto the hardness of a muscle was always estimatively determined by digital touching. The above mentioned fact caused me to look for means of expressing such changes in hardness more accurately in measure and number, as an approximate determination would not do here.

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[1]) Chem. Centr. 1900. I. 1084. I hope to communicate more analogous cases of intramolecular oxidation later on.

A communication by J. von Uexküll[1]) on the 18th of April last "Die Verdichtung der Muskeln", led me to a separate description of my investigations about the determination of hardness in muscles. In this communication he says: "wir besitzen zwar kein geeignetes Instrument, um das Hartwerden der Muskeln zu messen", while he winds up as follows: "Ich habe geglaubt, auf diese wichtige, aber allzusehr vernachlässigte Eigenschaft der Muskeln hinzuweisen, in der Hoffnung, dass sich jemand findet der einen brauchbaren Apparat konstruiert, um die Muskelverdichtung unabhängig von der Muskelverdickung zu registrieren."

For many decades together mineralogists have made determination of the hardness of materials, in which a number of methods were employed, which, however, in that form could not be applied to living objects. The literature only gathers for what is called hardness in general, data, for which I refer to some authors[2]) in behalf of those who wish to become more thoroughly acquainted with the subject.

Hardness is a collective idea, including and typifying an amount of qualities: cohesion, elasticity, plasticity, gliding, splitting and fracture. It is on the value which in a concrete case is assigned more especially to one of the qualities mentioned, that depends the general definition which shall be given of hardness. For living objects gliding, splitting and fracture need not be taken into account. I desist from a more detailed separate description of the three remaining qualities: cohesion, elasticity and plasticity. But if these three qualities are paid attention to, Auerbach's[3]) definition of hardness will no doubt be agreed to: "Härte ist eine Art von Festigkeit, nämlich der Widerstand gegen die Bildung von Unstetigkeiten oder dauernden Deformationen beim Drucke zweier sphärischer Oberflächen gegen einander, und kann Eindringungsfestigkeit genannt werden . . . Sie ist quantitativ durch den Grenzeinheitsdruck im Mittelpunkte der Druckfläche bestimmt."

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[1]) J. v. Uexküll. Die Verdichtung der Muskeln. Originalmitteilung. Zentralblatt für Physiologie. Bd. XXII N°. 2.

[2]) H. Rosenbusch und E. A. Wülfing. Physiographie Allgemeiner Teil. Stuttgart 1904.

G. Tschermak. Lehrbuch der Mineralogie. Wien 1905.

Egon Müller. Ueber Härtebestimmung Inaug. Dissert. Jena 1906.

[3]) F. Auerbach. Kanon der Physik pag. 119. Leipzig 1899.

The determination of hardness may give absolute and relative values. Among the methods of relative determination that of THOULET[1]) appeared to be useful also to determine the relative hardness of living objects.

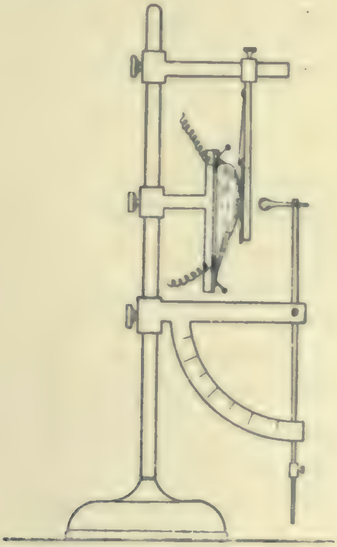
THOULET examined the elasticity of rocks and found points of comparison for this in the number of reflections and in the angle of reflection of a swinging ball suspended in the air. Indeed, if we drop a hard, elastic object upon an other, it will among others depend on the hardness of the surface that is hit, how often and how far the reflection will take place. Now, if this principle is put into practice with a much weaker object like a muscle, these reflections will, though in a smaller degree, yet take place in the same manner, which is corroborated by experience.

The angle of reflection of a falling globule resp. the number of its perceptible taps or reflections depends:

1. on the cohesion, elasticity and plasticity of the falling globule.
2. on the cohesion, elasticity and plasticity of the object hit, in this case the muscle.

Now as in case of comparing determinations sub 1 remains constant, sub 2 must be the only changeable, determinative factor.

The investigation takes place as follows with an apparatus that I call physiological sclerometer.



Physiological Sclerometer. Schematic drawing.
Fig. 1.

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[1]) M. J. THOULET. Recherches sur l'élasticité des mineraux et des roches. Comptes rendues de l'Academie des sciences. Paris. Tome 96. 1883.

A small pendulum with a fixed turning-point, of which the short beam points upwards to a height of 6 cM., bears on the head of that short arm a handled glass-tear, whilst the other longest arm, 15 cM. long, is provided with a small, movable weight, in consequence of which the moment of that lever-beam is variable. By this way the force with which the head of the glass-tear hits the object, can be made variable. In order to enlarge the living force of the falling object, the pendulum may be given different initial amplitudes. On a scale along which the longest lever moves, this height of falling is expressed in degrees.

The muscle to be examined is by means of its two tendons attached to a somewhat rough surface, here a hard cork-plate, to prevent removal of the muscle by the falling, tapping object. It is advisable in this way to determine the hardness of a muscle under isometric conditions, for, when the muscle is examined under isotonic conditions, the data are getting far less trustworthy, as : 1. in shortening the muscle, the point that is to be touched, by not shortening changes its place and can only be found back by marking it beforehand with colouring matter; 2. the weight necessary for the stretching seems to make the differences in hardness smaller.

The number of times that the glass-tear is reflected by the muscle before it is at rest, is determined either acoustically or by means of photography. The photographic registration has this advantage that at the same time the width of the reflections can be followed.

The photographic registration takes place as follows : the light of an arc-lamp of 220 volt and 10 ampère is by a condenser more or less pressed together into a cone of rays having its focus in a diaphragm. This focus in its turn serves as a source of light and procures by means of a biconvex lens thè parallel bundle of rays emitted. This bundle reaches the removable slit of a small box which in its opposite side is provided with a cylinder-lens of GARTEN. The light that has entered through the slit, is by the cylinder-lens, which is graduated, nipped together to an horizontal line of light, which falls through another slit into a second larger box on a drum that is in rotatory motion and to which sensitive bromide-paper of Dr. SCHÄEFFLEN is fixed. The box containing the drum is impenetrable to light by means of light-free axes. This drum is moved on by a clock, as it is used in the telegraphic Morse-apparatus. Between cylinder-lens and the larger box is placed the long beam of the lever of the sclerometer which during its movements removes a silhouette on the sensitive silver-paper.

The following experiment was made : M. sartorius of Rana temporaria is alternately passed through by an electric current, arising by a potential difference of 1.4 volt. For this purpose two brass plates serving as electrodes for the current, had been sunk in the cork sub-stratum of the muscle, whilst by means of a commutator the direction of the current can be changed. At the beginning of the experiment the anode is found at the distal tendon; afterwards the current is turned and ends in its original direction. In the subjoined table occur the widths of the first 4 reflections in mM.

Reflection	Anode at the distal tendon		Kathode at the distal tendon				Anode at the distal tendon	
I	52.5mM.	52mM.	54mM.	53 mM.	54mM.	53mM.	50 mM.	50 mM.
II	29.5	29	31	30	31	31	29.5	29
III	21	21	23	22.5	22	22	20.5	21
IV	16	16	18	17	17	17	16	15.5

The following table gives the difference between the M. sartorius of Rana temporaria through which a galvanic current has passed and another through which it has not passed.

Reflection	Muscle through which no current is passing			Muscle through which a current is passing Anode at the distal tendon			
I	40 mM.	40.5mM.	40.5mM.	45 mM.	43 mM.	43 mM.	43 mM.
II	24.5	25	25	28	26.5	26	27
III	16.5	17	17	18	17.5	17	17.5
IV	11	11	11	12	11.5	11.5	12

That abundant moistening of a muscle with mutually equimolecular salt-solutions, the effect of which on the autotonus is antagonistic, can alter the hardness, appears from what follows, also holding good for the M. sartorius of Rana temporaria.

Reflection	Moistening with kaliumchloride				Moistening with natriumchloride					Moistening with kaliumchloride			
	mM.	mM.	mM.	mM.	mM.	mM.	mM.	mM.	mM.	mM.	mM.	mM.	mM.
I	48	42.5	41	40.5	40	37	33	38	38	38	38	38	39
II	33	25.5	25.5	26.5	25.5	24.5	22.5	24	23.5	23	22	22	23
III	24	17	16.5	17	16.5	17.5	16.5	16	15	15	14	14.5	14.5
IV	17.5	11	10.5	11.5	12	12.5	12	10	10	9.5	9	9	9.5
V	12.5	8.5	8	8	9	9	9	7.5	8	8	8	8	8
VI	9	7	7.5	7.5	7.5	8	8	7	7	7	7	7	7

For a plain muscle whose fibres are parallel as in the M. sartorius of Rana, the above method is a rather fit one, though not in all respects. For the shortening of the muscle is accompanied by a thickening, in consequence of which the distance between muscle and glass-tear is somewhat altered. This is not of much importance for the thin M. sartorius, but if the experiment is made with muscles like M. gastrocnemius, this difference becomes more considerable, so that it ought to be taken into account. Besides the peculiar rounding of the surface of the muscle may somewhat alter the place of tapping, and in the end the glass-tear sometimes slightly sticks to the muscle, when we are tapping with a small load on the longer beam of the lever.

To meet these and similar drawbacks the following alterations were made. Between muscle and tapping glass-tear is inserted a thin glass plate, which intercepts the taps and transfers them to the muscle. In these circumstances the angle of reflection resp. the number of collisions depends on:

1. the cohesion, elasticity, plasticity of the tapping glass-tear;
2. the cohesion, elasticity, plasticity of the inserted glass plate;
3. the cohesion, elasticity, plasticity of the object to be examined.

Sub 1 and 2 remaining constant, only sub 3 is variable.

In order to come to a determination, the following technical precautions ought to be taken into consideration. The glass plate, a covering glass, is hanging, slightly movable, on a couple of rather stiff horse-hairs. Now the muscle presses this glass plate against an immovable metal fork, so that the glass plate can only make movements in one direction, viz. in the direction of the muscle, as soon as the glass plate is hit by the tapping glass-tear. At every touch of the covering glass the glass globule produces a clearly audible tap. The number of taps is easy to count and is a pretty accurate measure for the number of real movements of the glass, without agreeing with it in number. In proportion as the covering glass is pressed more against the fork by a harder mass of muscles, the oscillations of the little lever will retain a longer and wider amplitude and will also occur more frequently.

The height of falling is of great importance for the effect that is to be reached, in the first place with respect to the number and amplitude of the oscillations.

When at different heights of falling the number of corresponding audible taps is counted for the same muscle, the latter may be represented by a curve, in which the ordinate renders the number of audible taps and the abscis the height of falling in degrees. The curve thus got shows a peculiar course.

The above experiment was made with a dead muscle, to avoid as much as possible all variable factors of the living object. These come into operation, as appeared from experiments, in which first a curve was produced by observations of a living muscle, and the next day a second curve could be formed from observations of the now dead muscle, which under a glass cover with saturated vapour of water and thymol-vapour was preserved resp. from desiccating and rotting. The values denoted by the curve are averages got from at least five observations each time, which did not materially differ from each other.

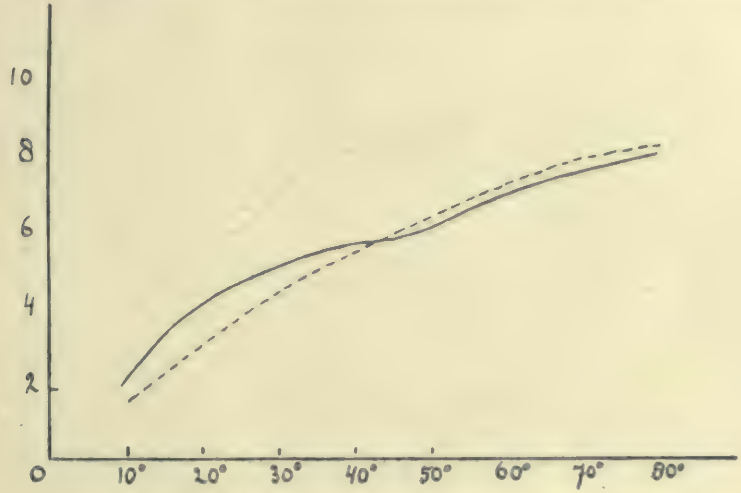

Fig. 2.

Hardness with regard to different heights of falling by a muscle in its dead and living situation.

——— = living muscle. ------ = dead muscle.

The ordinate gives the number of audible taps and the abscis the initial height of falling in degrees.

In different ways the hardness of a muscle can be made to undergo changes, which are either permanent, or which exist long enough for the determining investigation:

1. by making a galvanic current pass through a muscle;

2. by abundant moistening with equimolecular salt-solutions;

3. by faradaic excitement, either direct or indirect, so that the muscle is in tetanus;

4. by heating, resp. cooling.

An example of the two first mentioned manners was given before; one of the two other manners is as follows: a muscle is by indirect excitement with a faradaic current alternately brought to tetanus. At corresponding moments the determinations of hardness take place.

The subjoined table contains the width of the first 8 reflections which were reproduced photographically; at the same time the duration of these 8 reflections was calculated.

M. gastrocnemius of Rana temporaria.

	Normal muscle	Excited to tetanus	Not excited	Excited to tetanus	Not excited	Excited after rest
I	56 mM.	61 mM.	56 mM.	57 mM.	56 mM.	59 mM.
II	38	45	39	43	40	44.5
III	29	35	29	33	31	33
IV	22	28	22.5	26	23.5	26
V	17	22.5	17.5	21	18	21.5
VI	13	18.5	13	16.5	14	17
VII	11	15.5	11.5	13.5	12	13.5
VIII	9.5	12.5	10	11.5	10	11.5
	Duration of the first eight reflections.					
	4.4 sec.	4 sec.	4.3 sec.	4 sec.	4.3 sec.	4 sec.

From this it appears that in comparing the first 8 reflections not only the amplitude changes, but that also the time in which these oscillations take place, varies with the greater or smaller degree of hardness of the muscle. As the experiment progresses, it may be observed in the table that the heights of the reflections are getting larger also at the moments when the muscle is not excited. This must be connected with the changes in the constant state of contraction (autotonus), which arise in every fatigued muscle. That the muscle becomes really tired, is proved by the fact: 1. that the muscle visibly contracts less, 2. that changes in duration and height of the reflections diminish after repeated excitement, 3. that after the rest the effect of excitement agrees again with what was observed in the beginning of the experiment.

We add a tabulated statement of an experiment in which the muscle at the end of the experiment had become entirely inexcitable, as appeared from the absence of visible contractions, both for indirect and direct faradaic excitement, though still slight alterations in hardness appeared to be perceptible.

M. gastrocnemius of Rana temporaria
becoming inexcitable according to every-day parlance.

	Normal muscle	Excited	Not excited	Excited	Not excited	Excited
I	53 mM.	60 mM.	48 mM.	52 mM.	48 mM.	50 mM.
II	40	50	35	38	35	36
III	28	36	24.5	26	24.5	26.5
IV	21	27	17.5	18	17.5	19
V	15	21.5	13	14	13	15
VI	12.5	17	12	12.5	12	12.5
VII	10.5	13.5	11	11	11	11.5
VIII	10	11.5	10	10	10	10
	Total duration of the first 8 reflections.					
	5.4 sec.	5.2 sec.	5.2 sec.	5 sec.	4.4 sec.	4.8 sec.

M. gastrocnemius of Rana temporaria.

	Temperature in temperator			
	12.5° Celsius		56° Celsius	
I	49 mM.	49 mM.	50 mM.	50 mM.
II	38	39	41	41
III	27	27.5	31	30.5
IV	19.5	20	25	24.5
V	16	16	21	21
VI	13.5	14	18	18
VII	13	13	16	16
VIII	12	12.5	14.5	14.5
	Audible taps			
	7	7	10	10
	Total duration of the first 8 reflections in abscis-length			
	3.6 cM.	3.8 cM.	3.2 cM.	3 cM.

If a striated muscle is heated, it shortens: this is accompanied, as appears from the experiments, by changes of hardness. In order to trace this, the muscle in the sclerometer, instead of to a corkplate, was fixed to the thin copper bottom of a temperator, now serving as resting-surface. Through this temperator, as THUNBERG pointed out for the examination of the cold- and heat-points of the skin, alternately cold and hot water could be made to circulate. The copper bottom communicates the heat to the muscle; the temperature in the temperator and that which the muscle gets, will not soon be the same, but still is always in close connection with it.

As a demonstration I give here a couple of photographic reproductions of the oscillations of the beam of the sclerometer, as they were made, and from which among others the above table was partly derived. Fig. 3 gives the sclerometric reproduction of hardness of a muscle at a temperature of 12.5° C. in the temperator, whilst fig. 4 shows the reproduction when the same muscle is heated to 56° C. (See figs 3 and 4).

If a muscle is heated to not too high a temperature, a decrease of hardness manifests itself again after cooling, even though the muscle does not quite reach its original degree of hardness.

The subjoined table makes this clear.

M. gastrocnemius of Rana temporaria.

	Temperature in temperator						
	13° Celsius		61° Celsius			11° Celsius	
I	49 mM.	49 mM.	50 mM.	50 mM.	50 mM.	49 mM.	49 mM.
II	37	38	42	41	41	38	39
II	28	30	34	33	33	30	30
V	24	24.5	29	28	28	25	25
V	20	20	25	25	24	21.5	22
VI	17	17.5	22	22	21.5	18.5	19
VII	14	15	20	19.5	19	16.5	17
VIII	12.5	12.5	18	17.5	17.5	14.5	15
	Audible taps						
	10	10	15	16	16	13	13

A. K. M. NOYONS. „About the determination of hardness in muscles.”

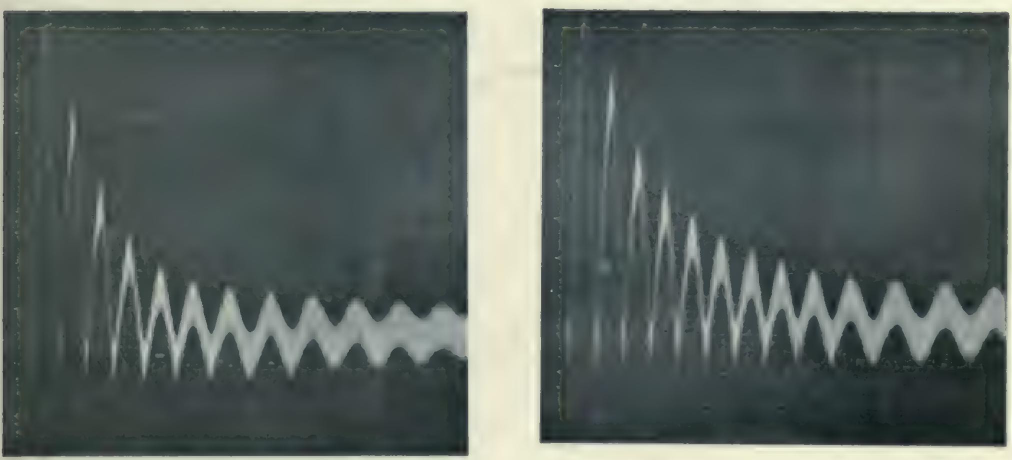

Fig. 3. Fig. 4.

Sclerometric reproduction of hardness:

at 12,5° Celsius. at 56° Celsius.

Such warming and cooling can be repeated a couple of times, whilst in proportion to this the number of reflections continues varying, provided the muscle be not for too long a time exposed to too high a temperature, as in this case a clearly perceptible permanent hardness will show itself.

Physiology. — "*On the structure of the ganglion-cells in the central nervous system of Branchiostoma lanc.*" (Second communic.)

By Dr. J. Boeke. (Communicated by Prof. G. C. J. Vosmaer).

(Communicated in the Meeting of May 31, 1908).

a. *The infundibular organ.*

The cells of the differentiated part of the ventral cerebral wall of Branchiostoma, which I described some years ago in these Proceedings[1]), and which was then called the *infundibular organ* on account of its place and the homology that could be drawn from that, are quite different in their structure from the other cells, of which I gave a description in my former paper[2]).

Among the authors, who in recent years have published researches on the central nervous system of amphioxus, Kupffer[3]) gives the same description of the cells as I gave in my paper in 1902, and only mentions the organ as consisting of long cylindrical cells with curved cilia and a clear hyaline protoplasm. Kupffer homologises the differentiated epithelium with the tuberculum posterius of the craniote embryos. Joseph[4]) only mentions the organ without adding anything to the description. Edinger[5]) who examined preparations stained after the method of Bielschowsky, calls it "das aus grossen Flimmer- und Sinneszellen bestehende Infundibularorgan", without mentioning on what is founded the opinion, that there are two kinds of cells to be found. In the drawings reproduced in his paper nothing is to be seen but a faint striation of the ventral wall of the brain at the place of the infundibular organ. According to Wolff[6]) there is a striking resemblance between the differentiated epithelium of the infundibular organ and the gelatinous tissue that we find in the central nervous system of the higher vertebrate animals, but evidently he has not seen much of the real structure of the tissue. Besides these statements nothing more is to be found about this part of the brain of amphioxus, and so we seem to be justified in giving an exact description of it here.

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[1]) Proc. Roy. Acad of Sc. of Amsterdam, Math. Phys. Cl. Meeting of April '07 p. 86.

[2]) Proc. Roy. Acad. of Sc. of Amsterdam, Math Phys. Cl. Meeting of April '02 p. 695.

[3]) Handbuch der Entwickelingslehre (Hertwig), Vol. 2, 3d part.

[4]) Verhandl. d. Anat. Gesellsch. 18. Vers. 1904.

[5]) Anat. Anzeiger, Bd. 28, 1906.

[6]) Biol. Centralblatt. Bd. 27, 1907.

To do this it is necessary to study first of all very thin carefully orientated median sections, as well as frontal and cross sections; the statements by EDINGER made it necessary to examine a great many BIELSCHOWSKY-preparations to form a correct opinion in this matter; hence we took so long for our research.

From the very early period at which the infundibular organ is regularly found and the constancy with which it appears, always in exactly the same form and structure, it is evident that it must play a distinct and important part in the animal's life. Already in larvae with only three primary gill clefts the differentiated epithelium is very obvious. Just where the narrow central canal opens into the wider part of the brain-ventricle, we see the ventral limit of the central canal rise slightly and sink again to the former niveau immediately after. This elevation is caused by the cells in the ventral wall growing out into long cylindrical elements, each cell bearing a long hair or cilium curving backwards, the cells lying regularly one beside the other.

It is an important feature in the development of the infundibular organ that the elongation of the cells first shows itself not in the median line but at the left side of the median plane; afterwards the cylindrical cells are also found at the right side. It is only at a much later stage that the long cells fuse in the median line and become one single mass. This and peculiarities in the course of the nerve-fibres springing from the cells in the full-grown organ, point to a bilateral origin of it.

The cylindrical elongation of the cells is the only change we find. There is no indentation at all of the wall of the brain in front of the organ to be found.

Already in very young animals we see in well-preserved and well-stained preparations that the cilia of the long cells point backward with a slight curve, the cilia of all the surrounding cells pointing forward, to the anterior neuroporus.

In older specimens we find the same state of things, but the cells get still more elongated, and the nucleus, now being small and spherical, is lying near the basis of the cell. All cells are directed backwards, that is to say, their free surface being turned craniad. (fig. 8).

For the topographical relations of the differentiated epithelium to the other parts of the brain I refer to my former paper (1902).

I can only state here in reference to the contradictory statement of EDINGER, that even in more developed and in full-grown specimens I never found another kind of cells in the organ nor an indentation of the brainwall in front of the infundibular organ (KUPFFER). In fig. 1 is drawn a median section of the full-grown organ, and here we see that the cells are not slanting any more, but are directed perpendicularly to the longitudinal axis of the body. In slightly younger animals one often finds the greater part of the cell still curved backward, while the upper part of the cell has assumed the perpendicular direction already (fig. 4*a*). The cause of this change must be sought in the different rate of growth of the surrounding tissue, the whole cerebrum becoming shorter, and changing from an oblong into a more rounded form.

As I mentioned before, the cells of the infundibular organ have all a backwards curved cilium; these cilia form a plume reaching to the narrow part of the central canal. In young animals being examined alive under the microscope the transparent tissue all round the brain ventricle allows the course of these cilia to be very clearly visible, and then the cilia of all the surrounding cells, pointing forward to the anterior neuroporus, appear as straight hairs forming a compact bundle which runs towards the neuropore, into which the hairs can be traced as long as it is open. The back end of this bundle of cilia is crossed by the cilia of the infundibular-cells.

The form of the cells in the full-grown animal is shown in fig. 4*b*. The neurofibrillar differentiation in the protoplasm of the cell, as I described it already in my former paper, the neurofibrillar network round the nucleus and the way, in which the neurofibrilla leaves the cell is in Fig. 3 clearly to be seen. The course of the nerve-fibres after they left the cell-body I could not trace much farther with a sufficient amount of certainty. They all seem to curve backwards (caudal), and from the study of frontal sections it was possible to draw the conclusion that the nerve-fibres springing from the cells form two bundles, each at one side of the median plane, running backwards, but getting lost to view between the other fibres of the medulla very soon after.

I never succeeded in finding an indentation of the ventral cerebral wall in front of the infundibular organ, as described by KUPFFER, although a large number of serial sections were examined. It is true, that, as I mentioned before, often the nuclei in the ventral wall in front of and behind the differentiated epithelium lie closer together than in the other regions and in a few cases the arrangement of these nuclei made the impression of a solid indentation. But upon closer examination I always found that this was only an apparent and no real indentation (infundibulum). Here one must be very careful not to draw any conclusions from a few series of sections. In a median section through the infundibular organ from one of my longitudinal series of a 47 mm. long Branchiostoma one would be inclined to draw the conclusion that there exists a groove-shaped indentation of the brainwall behind the organ, no trace of any indentation being found in front of it. So I think it dangerous to found a homology on this indentation, as KUPFFER did, and I adhere to the denomination "infundibular organ", as its structure and development have more resemblance with the epithelium in the saccus vasculosus of the ichthyopsidae, to which I gave the same name, than with the tuberculum posterius, which is still somewhat problematical.

b. *Shape and development of the brain-ventricle.*

I will here only mention those facts that are important for the comparison between the Branchiostoma cerebrum and that of the craniotes, and for the question whether the differentiated epithelium mentioned above may be homologised with the infundibular epithelium, or with the tuberculum posterius.

The second homology might be concluded from the drawing published by KUPFFER in 1894 and 1903, representing a median section through the cerebrum of a 2 c.m. long amphioxus. But this drawing seems to me not to represent the real state of things. Neither exactly orientated median sections (fig. 8) nor the median sections reconstructed from series of cross-sections (fig. 7) ever gave me anything like this drawing.

And yet it is in this case that the reconstruction-method must give an absolutely certain result. By this method we are able to correct entirely the deviations of the cerebral axis from the longitudinal axis of the body as they are found in almost every specimen. And as the cerebral vesicle has such a simple uncomplicated form this method gives us in every case an exact reproduction of the median section (which is certainly of the high value for the comparison of the brain KUPFFER ascribes to it), and at the same time allows us to get a sure knowledge of the width of the cerebral cavity. I give here three drawings of the median sections reconstructed from the cross-sections, one of a very young larva of 3,4 m.m. (fig. 5), one of a young amphioxus of 10 m.m. (fig. 6) and another of a specimen 21 m.m. long (fig. 7). All these are reconstructed from cross-sections of 5μ, magnified 800 to 1600 times, and afterwards reduced by means of photography. To fig. 5 I added the cross-sections lying on the spots indicated with *a*, *b*, *c*, *d*, to show the width and form of the cavity at the different spots. In fig. 8 I give the reproduction of a real median section through the brain of a specimen of about the same age as the one the reconstruction of which is given in fig. 7, to show how much they are like each other.

The reconstruction of fig. 5 shows, that even in very young larvae, (larvae of 1.5 to 2 m.m. give about the same picture), in which the brain is still larger in diametre than the spinal cord, there exists a dorsal dilatation of the cerebral cavity, which may be compared with the fourth ventricle of craniote embryos (fig. 5, 6, *VQ*). It represents a dorsal dilatation of the central canal (fig. 5*c*) and is connected with the anterior vesicle by a narrow part (fig. 5*b*). In all my specimens this connection of the ventriculus quartus with the anterior vesicle could be stated with absolute certainty, contrary to the well-known observations by Hatschek. Even in very young larvae the connection was very conspicuous. In the caudal part of the dorsal dilatation (fig. 5*d*) the midpart of the narrow fissure-like central canal is obliterated, so that this part of the fourth ventricle is separated from the ventral central canal which remains open. In older animals this obliteration proceeds craniad. The dorsal wall of the fourth ventricle is very thin consisting of one layer of flattened cells, but it is always visible even in very young larvae, if only the specimens are well-preserved.

In much older individuals, which passed through the metamorphosis long ago (fig. 6), the fourth ventricle is still very conspicuous and connected with the anterior vesicle by a narrow dorsal canal. The dorsal wall is still thin and membranous. The large dorsal ganglion-cells (vide my former paper) that are now developed to a certain extent, are still only visible at both sides of the median plane and do therefore not appear in the median section through the brain. Afterwards this peculiar group of cells is developed to such an extent (fig. 7, fig. 8), that they occupy the entire dorsal part of this region of the central nervous system, and so appear also in the median section. It is only then that the distinct fourth ventricle becomes indistinct, irregular, flattened, alters its shape and even disappears here and there. Then we find the peculiar irregular dilatations of the central cavity, described by Kupffer as "quere Schenkel" and "blasenförmige Erweiterungen". They are not segmental, are only of secondary importance, and are not to be compared with special parts and stages of development of the brain of craniote embryos.

After these statements I will add a few words concerning the cranial or rostral part of the cerebrum and the adjacent organs.

In his paper of 1906 EDINGER describes a new organ, the "frontal organ", lying in front of the brain and being innervated by a special nerve. I regret to say that I (no more than WOLFF in his paper of 1907) could find no trace of a frontal organ. Even after a most careful study of a number of individuals I can only find in the rostrum the often queerly shaped irregular mucous canals (Schleimcanäle) lying ventrally and dorsally of the chorda. They are never connected with the epidermis, but all receive very thin nerve-fibres from the first cerebral nerve.

Although the existence of a distinct nerve connecting the olfactory groove of KÖLLIKER with the brain, is denied by EDINGER, I could find it in my preparations as a bundle of fine nerve-fibres, connecting the sensory cells of the groove with the dorsal part of the brain. In all respects I could affirm the exact observations of DOGIEL (1903)[1]) both concerning the sensory cells in the olfactory groove and the nervous connection of them with the brain.

In the dorsal part of the cerebral wall I find a distinct commissural system, wherefrom bundles of nerve-fibres curve backwards (much like the fasciculus retroflexus of the commissura posterior of the craniotes) and a few fibres curve round forward. There are more systems of fibres to be found in the wall of the cerebral vesicle, but they are rudimentary and composed of only a few fibres. This is not the place to enter into details about these things. But when we take all this into account I think it is not permissible to consider the amphioxus-cerebrum as an "archencephalon" (KUPFFER), that has remained on a very low stage of development, but we must regard it as a degenerated cerebral system, which has become rudimentary in many of its parts, a brain which has many of the features of the brain of the ichthyopsides, but there are entirely lacking the organs of the side-line system (lens of the eye, ear, side-line) and because of that and of the fact, that the head has not developed as in the higher vertebrates, it is degenerated and rudimentary. In connection with this and with the elongation of the chorda the foldings of the cerebral vesicle do not appear. Even a plica ventralis does not exist. The infundibular organ remains in the niveau of the ventral cerebral wall.

Leiden. Histological part of the Anat. Kabinet.

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[1]) **Anatomische Hefte 21. Bd. 1903.**

DESCRIPTION OF FIGURES.

Fig. 1. Median longitudinal section of the infundibular organ of a Branchiostoma of 52 m.M. in length, 600 : 1.

Fig. 2. Cross-section through the same of a Branchiostoma of 54 m.M. in length, 600 : 1.

Fig. 3. The same as Fig. 1. Neurofibrillae stained with chloride of gold.

Fig 4. Cells of the infundibular organ, *a* of a Branchiostoma of 22 m.M. in length, *b* of 50 m.M. in length, *c* cross-section of the upper ends of the cells.

Fig. 5. Median section of the brain of a Branchiostoma larva of 3,4 m.M., reconstructed from cross-sections.

Fig. 6. The same of a specimen of 10 m.M. long.

Fig. 7. The same of a specimen of 21 m.M. long.

Fig. 8. Median section through the brain of a Branchiostoma of 28 m.M. in length.

Mathematics. — "*About difference quotients and differential quotients*". By Dr. L. E. J. Brouwer (Communicated by Prof. D. J. Korteweg).

(Communicated in the meeting of May 30, 1908).

Different investigations have been made which are very completely summed up in the work of Dini: "Grundlagen für eine Theorie der Functionen einer veränderlichen reellen Grösse" Chapt. XI and XII, on the connection between difference quotients and differential quotients, particularly on the necessary and satisfactory properties which the difference quotients must possess in order that there be a differential quotient. One however always regards in the first place these different difference quotients in one and the same point x_0 together, forming as a function of the increase of x the *derivatory function in* x_0. The existence of a differential quotient means then, that that derivatory function has a single limiting point in x_0 i.o.w. that in x_0 the right as well as the left *derivatory oscillation* is equal to zero.

Other conditions for the existence of a differential quotient are found when in the first place the difference quotient for constant x-increase Δ is regarded as a function of x and then the set of these functions for varying Δ is investigated. Let $f(x)$ be the given function which we suppose to be finite and continuous and let $\varphi_\Delta(x)$ be the difference quotient for a constant x-increase Δ. The different functions $\varphi_\Delta(x)$ form an infinite set of functions, in which each function is continuous. We shall occupy ourselves with the case that the set is *uniformly continuous*, i. e. that for any quantity ε, however small it may be, a quantity σ can be pointed out so that in any interval of the size of σ not one of the functions of the set has oscillations larger than ε. Concerning infinite uniformly continuous sets of functions there is a theorem that if they are limited (i.e., if a maximum value and a minimum value can be given between which all functions move) they possess *at least one* continuous limiting curve, to which uniform convergence takes place[1]).

We shall prove, that for the set of functions of the difference quotients of a finite continuous function, if it be uniformly continuous, follows in the first place the limitedness and furtheron for indefinite decrease of the x-increase the existence of only *one* limiting curve, so that holds:

Theorem 1. If a finite continuous function $f(x)$ has a uniformly continuous set of difference quotients, then it possesses a finite continuous differential quotient[2]).

To prove this we call ${}_{\delta}\varepsilon_{\Delta}(x)$ the size of the region of oscillation between x and $x+\Delta$ of the difference quotient for an x-increase δ. If we allow δ to assume successively all positive values, then it follows from the supposed uniform continuity, that Δ can always be chosen so small as to keep all values ${}_{\delta}\varepsilon_{\Delta}(x)$ below a certain amount as small as one cares to make it. If we thus call $\varepsilon_{\Delta}(x)$ the maximum of the values ${}_{\delta}\varepsilon_{\Delta}(x)$ for definite x and Δ, then $\varepsilon_{\Delta}(x)$ tends with Δ uniformly to 0.

We have fartheron if $\frac{p}{n}$ is a proper fraction:

$$\varphi_{\Delta}(x)=\frac{1}{n}\varphi_{\frac{\Delta}{n}}(x)+\frac{1}{n}\varphi_{\frac{\Delta}{n}}\left(x+\frac{1}{n}\Delta\right)+\ldots+\frac{1}{n}\varphi_{\frac{\Delta}{n}}\left(x+\frac{n-1}{n}\Delta\right) \quad (1)$$

$$\varphi_{\frac{p}{n}\Delta}(x)=\frac{1}{p}\varphi_{\frac{\Delta}{n}}(x)+\frac{1}{p}\varphi_{\frac{\Delta}{n}}\left(x+\frac{1}{n}\Delta\right)+\ldots+\frac{1}{p}\varphi_{\frac{\Delta}{n}}\left(x+\frac{p-1}{n}\Delta\right). \quad (2)$$

If we break up each of the n terms of the second member of (1) into p equal parts and each of the p terms of the second member of (2) into n equal parts, then the difference of those two second members can be divided into pn terms, each remaining in absolute value smaller than $\frac{1}{pn}\cdot\varepsilon_{\Delta}(x)$, so that the difference of $\varphi_{\Delta}(x)$ and $\varphi_{\frac{p}{n}\Delta}(x)$ remains smaller than $\varepsilon_{\Delta}(x)$ in absolute value.

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[1]) Compare Arzelà, "*Sulle funzioni di linee*", Memorie della Accademia di Bologna, serie 5, V, page 225.

[2]) We suppose the function to be given in a certain interval of values of the independent variable x.

So if we regard for any definite x all difference quotients the x-increases of which are equal to proper fractions of Δ, then the amount $\tau_\Delta(x)$ of their region of oscillation is smaller than $2\varepsilon_\Delta(x)$. The same holds for the region of oscillation of *all* difference quotients for definite x with x-increases smaller than Δ, because these can be approximated by the preceding on account of the continuity of f.

So if we allow Δ to decrease indefinitely, then also $\tau_\Delta(x)$ decreases indefinitely; as furthermore when Δ becomes smaller, each following region of oscillation is a part of the preceding, the limit of the region of oscillation is for each x a single definite value, to which uniform convergence takes place, which is the limit of the difference quotients, the *differential quotient*.

That this (forward) differential quotient cannot show any discontinuities, is evident as follows: If there were a discontinuity, then there would be a quantity σ which could be overstepped there for any interval by the oscillations of the differential quotient; but if the value of the differential quotient differs in two points more than σ, then there is also a difference quotient the values of which in those two points differ more than σ; so there would be for each interval, which contains the indicated discontinuity, a difference quotient with a region of oscillation larger than σ, i. o. w. the functional set of the difference quotients would not be uniformly continuous.

Out of the continuity of the forward differential quotient follows at the same time that the forward and the backward differential quotient are equal.

Analogously it is evident that also a point at infinity in the differential quotient would disturb the uniform continuity of the difference quotients; in this is at the same time included the limitedness of the difference quotients, for they would otherwise on account of the finiteness of f be able to tend to infinity only for indefinitely decreasing x-increase, but that would furnish an infinity point in the differential quotient.

Theorem 2. Of a function with finite continuous differential quotient the difference quotients are uniformly continuous.

Let namely ε be a definite quantity, to be taken as small as one likes. Now we may have each x included by an interval i in such a way, that the oscillations of the differential quotient within each of those intervals remain smaller than $^1/_2\,\varepsilon$. On account of the uniform convergence, evident from the formula $\varphi_\Delta(x) = f'(x + \vartheta\Delta)$, a Δ' can be pointed out in such a way that all φ_Δ for which $\Delta < \Delta'$ differ from the differential quotient less than $^1/_4\,\varepsilon$ for any x, thus have their oscillations below ε in the intervals mentioned. On account of the uniform continuity of f we may furthermore have each x included by an interval i' chosen in such a way that for all $\Delta \geq \Delta'$ the corresponding φ_Δ have within those intervals oscillations below ε only; to that end we have but to choose i' in such a way that the oscillations of f remain within the intervals below $^1/_2\, \varepsilon\, \Delta'$. If thus i'' is the smaller of the two quantities i and i', each x can be included by an interval i'' in such a way, that the oscillations of *all* difference quotients within it remain below ε, with which we have proved the uniform continuity of the difference quotients.

Theorem 3. If there is among the difference quotients of a finite continuous function a uniform continuous fundamental series with indefinitely decreasing x-increases, there exists a finite continuous differential quotient.

Let namely $\varphi_{\Delta'}(x), \varphi_{\Delta''}(x), \ldots$ be the fundamental series of functions under consideration, then for any quantity ε we can point out a quantity σ in such a way that $\varphi_{\Delta^{(\nu)}}(x+h) - \varphi_{\Delta^{(\nu)}}(x) < \varepsilon$ for any x, any $h < \sigma$ and any ν. If now the set of *all* difference quotients were not uniformly continuous, it would have to occur that for a certain Δ° not belonging to the fundamental series we should have $\varphi_{\Delta^\circ}(x+h) - \varphi_{\Delta^\circ}(x) > \varepsilon$. If we now approximate Δ° by a series $a_1\Delta', a_2\Delta'', \ldots$, where the a's represent integers, in such a way that $a_p\,\Delta^{(p)} < \Delta^\circ < (a_p+1)\Delta^{(p)}$, then also $\varphi_{\Delta^\circ}(x+h) - \varphi_{\Delta^\circ}(x)$ is approximated by $\varphi_{a_p\Delta^{(p)}}(x+h) - \varphi_{a_p\Delta^{(p)}}(x)$, which last expression always remains $< \varepsilon$ however large p may become, so that $\varphi_{\Delta^\circ}(x+h) - \varphi_{\Delta^\circ}(x)$ cannot be $> \varepsilon$, so the set of *all* difference quotients is uniformly continuous, and there is a finite continuous differential quotient.

Theorem 1 is applied when building up the theory of continuous groups out of the theory of sets, (where one remains independent of LIE's postulates), in a certain region finite and continuous functions of one or more variables occurring there, whose difference quotients are in a certain system of coordinates linear functions of the original functions.[1] As on account of the finiteness of the original functions there cannot be a region within which any quantity could be overstepped everywhere by one and the same difference quotient, the coefficients of the above mentioned linear functions remain within finite limits, the system of the difference quotients is uniformly continuous, and the differential quotients exist.

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[1] Comp. L. E. J. BROUWER, "*Die Theorie der endlichen continuierlichen Gruppen unabhängig von den Axiomen von* LIE", Atti del IV° Congresso Internazionale dei Matematici. It is the differentiability in one and the same system of coordinates of all the functions, which express the different infinitesimal transformations of a group, which is proved in this way.

Theorem 4. If the conditions of theorem 1 are satisfied and if the system of all second difference quotients (of which each is determined by two independent x-increases) forms a uniformly continuous system, then there exists a finite continuous "second differential quotient" which at the same time is the only limit of the above set of functions when both x-increases decrease indefinitely, and the differential quotient of the (first) differential quotient.

To prove this we call $\varepsilon'_\Delta(x)$ the maximum size of the regions of oscillation of the different second difference quotients between x and $x + \Delta$; then again $\varepsilon'_\Delta(x)$ tends with Δ uniformly to zero.

If we represent the difference quotient of $\varphi_{\Delta_1}(x)$ for an x-increase Δ_2 by $\varphi_{\Delta_1\Delta_2}(x)$ and if $\frac{p_1}{n_1}$ and $\frac{p_2}{n_2}$ are proper fractions then we have:

$$\varphi_{\Delta_1\Delta_2}(x) = \frac{1}{n_1 n_2} \sum_{k_1=0}^{n_1-1} \sum_{k_2=0}^{n_2-1} \varphi_{\frac{\Delta_1}{n_1}\frac{\Delta_2}{n_2}}\left(x + k_1\frac{\Delta_1}{n_1} + k_2\frac{\Delta_2}{n_2}\right). \quad . \quad . \quad (1)$$

$$\varphi_{\frac{p_1\Delta_1}{n_1}\frac{p_2\Delta_2}{n_2}}(x) = \frac{1}{p_1 p_2} \sum_{k_1=0}^{p_1-1} \sum_{k_2=0}^{p_2-1} \varphi_{\frac{\Delta_1}{n_1}\frac{\Delta_2}{n_2}}\left(x + k_1\frac{\Delta_1}{n_1} + k_2\frac{\Delta_2}{n_2}\right). \quad . \quad (2)$$

If we break up each of the $n_1 n_2$ terms of the second member of (1) into $p_1 p_2$ equal parts and each of the $p_1 p_2$ terms of the second member of (2) into $n_1 n_2$ equal parts, then the difference of those two members breaks up into $p_1 p_2\ n_1 n_1$ terms, each of which remaining in absolute value smaller than $\frac{1}{p_1 p_2\ n_1 n_2}\varepsilon'_{\Delta_1+\Delta_2}(x)$, so that the difference of $\varphi_{\Delta_1\Delta_2}(x)$ and $\varphi_{\frac{p_1\Delta_1}{n_1}\frac{p_2\Delta_2}{n_2}}(x)$ remains in absolute value smaller than $\varepsilon'_{\Delta_1+\Delta_2}(x)$.

So if we consider for any definite x all difference quotients whose x-increases are equal to proper fractions of Δ_1 and Δ_2, then the size $\tau_{\Delta_1\Delta_2}(x)$ of their region of oscillation is smaller than $2\varepsilon'_{\Delta_1+\Delta_2}(x)$, from which we deduce as above in the proof of theorem 1 the existence of one single limit, to which the convergence is uniform and which is finite and continuous.

If we now regard the difference quotient with x-increase Δ_2, on one hand for all φ_Δ's, whose Δ is smaller than Δ_1, and on the other hand for the (first) differential quotient, then the former all differ less than $\varepsilon'_{\Delta_1+\Delta_2}(x)$ from the limiting function just deduced, so also the latter, which can be approximated by them. This holds independently of Δ_1;

the difference for x-increase Δ_2 of the (first) differential quotient can therefore not differ more than $\varepsilon'_{\Delta_2}(x)$ from the just deduced limiting function which is thus differential quotient of the (first) differential quotient i.e. second differential quotient.

Theorem 5. If a function possesses a finite continuous second differential quotient, then the system of the first and second difference quotients is uniformly continuous.

To find namely an interval size i'' which keeps the oscillations of all second difference quotients everywhere $< \varepsilon$, we first take the interval size i, which keeps the oscillations of the second differential quotient everywhere $< \frac{1}{2}\varepsilon$; then a Δ'_1 and a Δ'_2 in such a way, that all $\varphi_{\Delta_1 \Delta_2}$, for which $\Delta_1 < \Delta'_1$ and $\Delta_2 < \Delta'_2$, differ along the whole course less than $^1/_4\varepsilon$ from the second differential quotient [1]; finally an interval size i' which keeps the oscillations of the function f everywhere $< {}^1/_4\, \varepsilon\, \Delta'_1 \Delta'_2$. For i'' we take the smaller of the two quantities i and i'.

Theorem 6. If there is among the second difference quotients of a finite continuous function with finite continuous differential quotient a uniformly continuous fundamental series, in which the two x-increases decrease indefinitely, then there exists a finite continuous second differential quotient.

Let namely $\varphi_{\Delta_1{}' \Delta_2{}'}(x)\,,\, \varphi_{\Delta_1{}'' \Delta_2{}''}(x) \ldots$ be the indicated fundamental series, then for any quantity ε a quantity σ can be pointed out in such a way, that $\varphi_{\Delta_1^{(\nu)} \Delta_2^{(\nu)}}(x+h) - \varphi_{\Delta_1^{(\nu)} \Delta_2^{(\nu)}}(x) < \varepsilon$ for any x, any $h < \sigma$ and any ν. If now the set of *all* second difference quotients were not uniformly continuous, then it would be possible for a certain $\Delta_1{}^\circ$ and $\Delta_2{}^\circ$ not belonging to the fundamental series, that $\varphi_{\Delta_1^\circ \Delta_2^\circ}(x+h) - \varphi_{\Delta_1^\circ \Delta_2^\circ}(x) > \varepsilon$. Let us now approximate $\Delta_1{}^\circ$ by means of a series $\alpha_1 \Delta_1{}'\,,\, \alpha_2 \Delta_1{}''\,, \ldots\ldots$ and $\Delta_2{}^\circ$ by means of a series $\beta_1 \Delta_2{}'\,,\, \beta_2 \Delta_2{}''\,, \ldots\ldots$, where the α's and β's represent integers, in such a way that

$$\alpha_p \Delta_1^{(p)} < \Delta_1^\circ < (\alpha_p + 1)\, \Delta_1^{(p)} \text{ and } \beta_p \Delta_2^{(p)} < \Delta_2^\circ < (\beta_p + 1)\, \Delta_2^{(p)},$$

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[1] The uniform convergence of all difference quotients is evident from that of the difference quotients, for which $\Delta_1 = \Delta_2$ (out of these the other can be approximated in the manner indicated in the proof of theorem 6); the latter is evident by developing the terms of $f(x + 2\,\Delta) - 2\,f(x + \Delta) + f(x)$ according to Taylor's series, in which we make the second differential quotient form the restterm; the terms preceding this restterm then destroy each other.

then also $\varphi_{\Delta_1^\circ\,\Delta_2^\circ}(x+h) - \varphi_{\Delta_1^\circ,\,\Delta_2^\circ}(x)$ is approximated by

$$\varphi_{\alpha_\nu \Delta_1^{(p)},\,\beta_p \Delta_2^{(p)}}(x+h) - \varphi_{\alpha_p \Delta_1^{(p)},\,\beta_p \Delta_2^{(p)}}(x)\,,$$

which last expression remains $< \varepsilon$, however great p may become, so that the first can neither be $> \varepsilon$,; so the set of *all* second difference quotients is uniformly continuous and there is a finite continuous second differential quotient.

Theorem 7. If there is among the second difference quotients of a finite continuous function a uniformly continuous fundamental series, in which both x-increases decrease indefinitely, the function possesses finite and continuous first and second differential quotients.

For, according to the above given proof of theorem 6 the whole system of the second difference quotients proves to be uniformly continuous, and out of the above given proof of theorem 4 this system proves to possess for indefinite decrease of the two x-increases one single finite continuous limiting function $f''(x)$ to which they converge uniformly. Let τ' be the maximum deviation from this limiting function of the second difference quotients, whose x-increases are smaller than Δ'_1 and Δ'_2, and let us regard the system ζ of all $\varphi_\Delta(x)$ whose $\Delta < \Delta'_1$, then all difference quotients with x-increase $< \Delta'_2$ of the system ζ lie between $f''(x) + \tau'$ and $f''(x) - \tau'$, from which may be deduced easily, that the system ζ is uniformly continuous, so that now first according to the proof of theorem 1 a finite continuous first differential quotient exists and then according to the proof of theorem 4 a finite continuous second differential quotient.

Analogous to the preceding are the proofs of the following more general theorems:

Theorem 8. If there is among the n^{th} difference quotients of a finite continuous function a uniformly continuous fundamental series, in which all x-increases decrease indefinitely, then the function possesses finite and continuous first, second, up to the n^{th} differential quotients; each p^{th} differential quotient is here first the only limit for indefinitely decreasing x-increases of the p^{th} difference quotients to which limit a uniform convergence takes place, and then differential quotient of the $(p-1)^{\text{st}}$ differential quotient.

Theorem 9. If a function possesses a finite continuous n^{th} differential quotient, then the system of the first, second, up to the n^{th} difference quotients is uniformly continuous[1]).

Theorem 10. If $n_1, n_2, n_3 \dots$ is an infinite series of increasing integers and if of a finite continuous function the systems of the n_1^{st}, of the $n_2^{\text{nd}} \dots$ difference quotients are uniformly continuous, then the function has all differential quotients and these are all finite and continuous.

Theorem 11. A finite continuous function of several variables, among whose difference quotients of the n^{th} order there is for each kind a uniformly continuous fundamental series in which the increases of the independent variables decrease indefinitely, possesses all differential quotients up to the n^{th} order; these finite and continuous differential quotients are first each other's differential quotients in the manner expressed by their form, where the order of succession of the differentiations proves to be irrelevant, and then each differential quotient is the only limit of the corresponding difference quotients for indefinitely decreasing increases of the independent variables, to which limit a uniform convergence takes place.

Theorem 12. If a function of several variables possesses all kinds of n^{th} differential quotients and if these are finite and continuous, then the system of the 1st, 2nd up to the n^{th} difference quotients is uniformly continuous.[2])

Finally the observation, that what was treated here leads infinite differentiability back to continuity in a more extensive sense, and in this way may somewhat explain, that for so long all finite continuous functions were supposed to be infinitely differentiable, and may somewhat justify that so many wish to limit themselves in natural science to infinitely differentiable functions.

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[1]) To prove the uniform convergence of the n^{th} difference quotients for equal independent x-increases we break off just as for theorem 5 the Taylor development at the n^{th} term and we apply the formula:

$$n^a - \binom{1}{n}(n-1)^a + \binom{2}{n}(n-2)^a \dots\dots = 0$$

(n and a integers; $a < n$).

[2]) To prove the uniform convergence of the n^{th} difference quotients with equal independent increases $\angle$ (these $\angle$ indefinitely decreasing) we develop the elements of such a difference quotient according to TAYLOR's series, in which we make the n^{th} differential quotients form the restterms. The terms preceding the restterms then fall out and of the restterms one kind converges uniformly to the differential quotient corresponding to the difference quotient considered and the other converge uniformly to zero.

Microbiology. — "*Fixation of free atmospheric nitrogen by Azotobacter in pure culture. Distribution of this bacterium*" By Prof. M. W. Beijerinck.

(Communicated in the meeting of May 30, 1908).

When carbon hydrates are used as source of carbon in *Azotobacter* cultures, there existed until now some doubt whether the then occurring fixation of free nitrogen was originally effected by *Azotobacter* itself or by other bacteria found in symbiosis with it, because *Azotobacter* in pure culture with carbon hydrates and free nitrogen only, does not show any considerable development.

For this reason I was formerly of opinion that in such cultures *Bacillus radiobacter*, a species closely allied to the bacteria of the Papilionaceae, and which is never absent in accumulations of *Azotobacter*, would be the real cause of the nitrogen fixation. ¹).

Continued research, however, rendered this supposition more and more improbable, and the facts which are now to be stated have proved beyond any doubt that the said faculty belongs indeed to *Azotobacter* itself.

These facts have regard to the very peculiar relation between *Azotobacter* and the salts of the organic acids, more in particular to calcium malate.

1. *Calcium malate as source of carbon.*

When into a wide Erlenmeyer jar a nutrient liquid is introduced of the composition: 100 tap-water, 2 calcium malate, 0.05 K^2HPO^4, with addition of some 10—20 cM^3 canal-water, or as much soil for infection, care being taken that the layer of liquid in the jar be not thicker than 2—5 cM, on cultivation in a thermostat at 30° C., usually after 2 or 3 days ²) a floating *Azotobacter* film appears, consisting of strongly motile individuals, and relatively soon obtaining a considerable thickness. Hereby so much calcium carbonate is produced that it forms a closed, floating layer, so to say a cover, on the surface of the liquid.

If some of this film is inoculated into another jar containing the same medium, corresponding phenomena are seen when the culture

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¹) These proceedings of March 1901. Centr.bl. f. Bact. 2te Abt. Bd. 9 pg. 1, 1902. Archives Néerl. (2) T. 8 p. 190 and 319, 1903.

²) Especially in spring and autumn these experiments succeed. In summer and winter *Azotobacter* seems sometimes absent in the said quantity of water.

conditions are alike. At first sight already, there can be no doubt but under these circumstances fixation of considerable quantities of nitrogen must take place, and chemical analysis proves that this is really the case.

The microscopic image of the *Azotobacter* growth in the malate commonly shows smaller individuals of greater motility than the formerly described forms which are obtained in the mannite solutions. They keep about the middle between *A. chroococcum* and *A. agilis,* and remind strongly of a variety found in America, which has received the name of *A. vinlandi.* The plate cultures of such a malate accumulation again prove not to be pure but to consist of the usual mixture of non spore-forming species. They are best grown on a medium of the composition: 100 tapwater, 1 calciummalate, 0.05 K^2HPO^4, 1 to 2 agar, on which the *Azotobacter* colonies become already visible after 12 hours at 30° C., which is not the case with any other species of microbes known to me. As these plates are somewhat cloudy by the produced calciumphosphate and the imperfectly dissolved malate, it is desirable to mix the ingredients in the way as follows. Into a culture tube are first introduced some drops of a neutral, concentrated solution of kaliummalate and herein are dissolved both the calciummalate and the kaliumphosphate, with a little water to dilute, but the smallest quantity possible, as the dissolving power of the kaliummalate is much stronger in the concentrated than in the dilute solution. Then the contents of the tube are mixed with the agar solution.

The malate plates prepared in this way have proved to be better for the growth of *Azotobacter* germs than the mannite and glucose plates, so that of a definite number of germs there develop more to colonies on the former than on the latter. Hence it has become possible more exactly to compute the number of individuals of our species present in a sample of soil than after the old method, to which circumstance we return below.

Before going further I wish to notice the following concerning other salts of organic acids as carbon food for *Azotobacter.*

Except with calciummalate there could be obtained an abundant or moderate growth with calciumlactate, calciumacetate and calciumpropionate, particularly when using canal water for the first infection. It was remarkable that the transport of a malate culture into lactate appeared to succeed nearly as well as of malate into malate, while even relatively rich crude cultures in propionate- or acetatesolutions, obtained directly from soil or water when inoculated into corresponding media, hardly grow on, if at all. This fact is the more remarkable when we consider that by inoculation of a malate film into propionate or acetate as abundant cultures are obtained as in the said crude cultures in these media. But if it is tried to continue such cultures by re-inoculating anew into propionate or acetate they also soon lose their power of growth. From this we see that the preceding culture conditions to which the inoculation material has been subjected, are by no means indifferent to the vitality of the following generations, which are evidently very easily weakened and then nearly quite lose the faculty of fixing nitrogen. The importance of this fact cannot be denied and certainly deserves a nearer examination.

Calciumcitrate, calciumtartrate and calciumsuccinate, with either garden soil or canal water for infection, give but slowly a moderately developed bacteria film but it grows during a very long time. The film on the citrate is rich in spirilla and the *Azotobacter* form found in it differs in many respects from the ordinary varieties. In all these cases the quantity of bacteria grown during the first 2 or 3 weeks, is still too slight to necessitate a determination of the nitrogen, and could by a rough comparison with former computations be valued at some tenths of milligrams N_2 per gram of the dissolved lime salt. After a long time however, the fixation of nitrogen with these salts is also considerable.

With calciumglycolate in absence of nitrogen compounds no growth of microbes could be observed at all.

2. *Quantity of the fixed nitrogen.*

Neglecting for the moment the volatile acid, to which we shall return below, the analysis of the cultures is performed as follows.

The whole quantity of the liquid, in which are present the calciumcarbonate formed by oxidation from the malate or the other organic salt, besides the as yet not decomposed malate, the salt of the volatile acid, and the bacteria, is treated with a known quantity of normal hydrochloric acid by which the carbonic acid is expelled on heating; a then following titration with normal alkali and phenolphtaleine as indicator, shows how much calciumcarbonate is produced and consequently how much of the organic salt is oxidised.

After addition of a little sulphuric acid the liquid is evaporated to dryness and after KJELDAHL's method examined on nitrogen, while in each of the materials used the rate of nitrogen is stated separately. The calciummalate of MERCK, Darmstadt, proved nearly free from nitrogen.

Now follows a table of some analyses [1]) which give an idea of the amount of nitrogen fixed through *Azotobacter,* when organic salts are used as carbon food. (See table).

These numbers show that the amount of nitrogen which can be fixed in the crude culture is at most 4.9 and 2,8 m.g. per gram of oxidised calciumsalt, obtained respectively with calciumpropionate and calciumacetate (experiment 10 and 11), while, per gram of calciummalate was fixed about 2,6 m.g. (experiment 2), and per gram of lactate 1,8 m.g. (experiment 9). It seems that the fixation goes on more rapidly at the beginning than later in the course of the experiment, whence it follows that when little of the organic salt is used proportionately more nitrogen is fixed than by larger amounts. This should be taken into consideration in judging the favourable results obtained with propionate and acetate, for then solutions were used with only 1°/₀ of the salt. As to these salts, they have proved to be in general an unfavourable source of carbon for *Azotobacter* if the *rapidity* of the growth is taken as indicator of the process, and only then to be able to give good results, when for the inoculation, cultures in malate solutions are used, in which a certain variety of our species is present. But also then, as observed above, already at the first passage from acetate into acetate the growth stops almost entirely. Pure cultures of *Azotobacter* develop hardly at all [2]) in solutions of calciumacetate and natriumacetate, whatever may have been the conditions to which these cultures were previonsly subjected. Propionates and lactates still require a nearer investigation.

Of calciummalate, on the other hand, it has decidedly been proved that not only the crude cultures succeed very well and fix much nitrogen even at repeated passages in the same medium, but that this also holds good with regard to the pure cultures of *Azotobacter*. This is the first case in which I got the certainty that no other microbes are wanted, neither in the medium nor in the infection materials, but *Azotobacter* alone to cause the said phenomena. Various authors surely have repeatedly described the fixation of free nitrogen in pure cultures of *Azotobacter*, among others of late with respect to the acetates, but never had I been able to confirm the accuracy of these statements until I made a systematic investigation with calciummalate, a salt which had never before been used to this end, although I had already called attention to it as an excellent source of carbon for *Azotobacter* in my papers of 1902.

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[1]) I owe to Mr. D. C. J. Minkman, assistant to my laboratory the determinations here referred to.

[2]) The different varieties behave, however differently and some will begin to grow but the growth soon ceases.

It must be allowed that the amount of fixed nitrogen in these pure cultures is not considerable, about 1.5 m.g. for each gram of oxidised malate, but perhaps here too, will be observed a greater production if only the very young cultures are examined; then, however, only little of the salt can be oxidised and the absolute quantities will of course be small.

It seems not superfluous here to call to mind that it is by no means the same whether a known amount of calciummalate be absorbed from a dilute solution or from a more concentrated one. In the latter case the malate will be more easily assimilable for the *Azotobacter* cells, which will induce a stronger oxidation and thus an increased oxygen assimilation in equal times, so that the tension of the oxygen in the liquid will be less than in the less concentrated solutions. As the growth of *Azotobacter* seems favoured by this lower tension, and in any case, a rather strong concentration of the carbon food proves favourable to the process of nitrogen fixation *in absolute quantity* this circumstance has been taken into consideration in all the experiments. Further, we did not always wait for the moment at which the malate had disappeared from the medium, but commonly it was much earlier subjected to the analysis for the reason mentioned above.

The observation that calciummalate can, glucose, cane-sugar and mannite on the other hand, cannot form the starting point for nitrogen fixation in liquid pure cultures, while yet the said carbon hydrates are in the crude cultures much more productive and may even give gains of nitrogen of 7 m.g. per gram of decomposed sugar, gives rise to the supposition that these carbon hydrates must previously be changed by other bacteria into organic acids and that these, at the moment of their production, serve as carbon food for *Azotobacter* and primarily cause the fixation of the nitrogen.

Of course it cannot be malic acid which hereby originates from the sugar; but the important growth of *Azotobacter* to which also the acetates, the propionates and lactates may give rise, suggest the question whether perhaps the acids of these salts may be first produced from the carbon hydrates and then govern the nitrogen fixation.

It is to be remarked that as well in the malate as in the lactate cultures slight amounts occur of a volatile acid, which will perhaps prove to be acetic acid, although it is has not been positively demonstrated by means of BEHRENS' uranylanatrium-acetate reaction. It is of importance to know that this volatile acid is not only found in the crude, but also in the pure cultures of *Azotobacter*, so that it is certainly a product of this species itself.

In order to ascertain the amount of the volatile acid and the corresponding quantity of decomposed malate, it is supposed in the table to be acetic acid only and produced after the formula:

$$2C^4 H^4 O^5 Ca + 2O^2 = C^4 H^6 O^4 Ca + Ca\,CO^3 + 3\,CO^2 + H^2 O$$

Calciummalate Calciumacetate.

But it may also be formed without access of oxygen. The volatile acid is determined by distillation with sulphuric acid and silver sulphate and titration the distillate with normal alkali.

From the table we see that in the crude cultures nitrogen can without doubt be fixed with calcium acetate as carbon source. In truth we have not succeeded in effecting the same in pure cultures, but now that we have the certainty that *Azotobacter* alone, with malate as carbon food, is able to fix nitrogen, it must be admitted that this also holds good for the acetate cultures, although it is not clear of what nature is the assistance which other bacteria thereby must necessarily lend. Besides it should be noted that the fixation of nitrogen in the pure cultures, also when malate is used as carbon food, is less considerable than when other bacteria, too, can live on this substance at the same time.

3. *Distribution of Azotobacter in the soil.*

Earlier, already, I showed that it is possible to detect a few *Azotobacter* colonies among the thousands of those of the other species, when fertile garden soil is sown on mannite-kalium-phosphate plates. The use of calciummalate instead of sugar has proved to be of importance for the examination of the soil in this direction. First it should, however, be observed that no solid or liquid medium ¹) could be found on which all the germs of *Azotobacter* sown out really develop into colonies. Thus, by sowing about 2400 germs (determined by microscopic counting), on various culture plates, 50, 12, 1, 30, 8, 20, 10, 20 and 75 colonies developed so that the growth in percents was only 2, 0.6, 0.5, 0.3, 0.3, 0.8, 0.4, 0.8 and 0.3. In another experiment were obtained of 10.000 germs sown on glucose-calcium-malate plates, 20, 25 and 48°/₀, and on calcium-kaliummalate-plates 32.5, 36 and 65°/₀. But in other cases, on agar plates with malate only the results were much better. The germs had

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¹) The use of thin layers of liquid media for colony culture of microbes has been described in Centralblatt f. Bacteriologie, 2te Abt. Bd 20, 1908, p. 641.

been shaken up in sterile tap-water or in malate solutions, of which 1 cm^3 was spread over the plate, care being taken that the water was quite taken up into the agar by its power of imbibition, which is easily effected by softly heating the plate so that the superfluous water evaporates.

We see from these data that *commonly* only a small part of the sown germs comes to growth. Whether perhaps the water itself has a deadly influence on some individuals, or that their death is caused by their passing on the solid medium, could not yet be made out by experiment. Thus, although there be ground to allow that more germs occur in the soil used than are found, the possibility exists that by continued investigation the experiment may be made so as to exclude that source of error.

But in spite of the uncertainty of the method the following result could be stated. By sowing a small quantity, for instance less than $\frac{1}{20}$ gram of garden soil on calciummalate-kaliumphosphate 1°/₀ agar, after 24 hours at 30° C. commonly no *Azotobacter* is observed, but a moderate number of moist colonies of about 1 mm. in diameter, first draw attention by their extension and prove to consist of different varieties of *Bacillus megatherium*, containing many spores. They dont cause any considerable oxidation of the malate and as the colonies no more grow after the second day, they evidently develop at the expense of the traces of nitrogen compounds which at first are present in the plates. After the second day a great number of *Streptothrix alba* appear. This microbe is so common in all the examined samples of soil that there can exist no doubt as to its either favourable or pernicious influence on the fertility; but the nature of this influence is as yet wholly unknown.

In a still later stadium the surface of the plate becomes covered with numerous relatively small colonies of bacteria, among which some species immediately draw attention by their extension and commonness.

The oxidation of the malate by all these microbes is slight, so that even after weeks the plates contain but little calcium carbonate, which seems almost entirely produced by the said larger colonies and by *Streptothrix*. All these species seem not to oxidise at all, or perhaps it is more accurate to say, not to oxidise any more after the last traces of fixed nitrogen have been assimilated. As to *Streptothrix*, from its relatively vigorous oxidising power it follows by no means that this should be associated with fixation of nitrogen; this species surely does not possess that faculty. If for the experiment soil is used shaken from the roots of garden-plants, which are no Papilionaceae, the result is fairly the same; perhaps the number of the above mentioned oxidising forms is more numerous, but this is still doubtful.

Otherwise, however, is the result when the soil is examined which adheres to the roots of clover, pease, and beans when these plants are cautiously dug up. When the soil adhering to such roots is rubbed fine and after dilution in water sown on a malate plate we find, after a period of 2 days at 30° C., first that the said oxidising colonies have very abundantly developed. But, besides, among these colonies much larger ones are distributed, which oxidise much more vigorously and prove to belong to *Azotobacter*, which shows that a distinct relation exists between the distribution of this genus and the said Papilionaceae. Whether this relation will appear to be universal and what may be its signification, further experiments have to decide.

Chemistry. — "*Rapid change in composition of some tropical fruits during their ripening.*" By H. C. Prinsen Geerligs.

(Communicated in the meeting of May 30, 1907).

Some tropical fruits which as a rule are gathered in a green and immature state and allowed to ripen afterwards, accomplish this ripening process so rapidly that within a few days they become tender, well-flavoured and palatable, thus offering a good opportunity for studying the still somewhat mysterious problem of the after-ripening of fruits.

I. Phenomena during after-ripening.

a. Banana (Musa).

As a rule the bunches of bananas, which contain fruits in various stages of maturity, are cut from the plant as a whole when all the fruits are still green and are hung up to ripen. At the moment when the bunch is cut none of the bananas are fit for food; they are hard, tasteless and flavourless, the skin is thick, contains much latex and tannin and adheres to the fleshy part. After a few days the skin becomes thin and yellow and can easily be detached, whilst the edible matter is now tender, sweet and well-flavoured. A couple of days afterwards the fruit is unpalatable again owing to overripeness and decay which change it into a soft mass.

This after-ripening is accompanied by a considerable loss of weight as is shown by the following figures.

20 bananas broken from the bunch in a green state were placed in a relatively cool spot (28° C.) and weighed daily.

The average weight per fruit was:

after	0	1	2	3	4	5	6	7	days
	145	143	142.5	142	141	139	138	137	grammes.

Further, 10 green bananas of another variety were placed under a glass bell jar into which a current of air free from carbonic acid was introduced. The air leaving the bell jar was made to pass through a drying apparatus and a Liebig potash bulb, which latter was daily weighed.

The fruits weighed originally	502.5	grammes
and after 4 days only . .	487.0	,,
therefore lost in weight . .	15.5	grammes

The weight of the potash bulb increased

the first day by	0.065	grammes
the second day by	1.455	,,
the third day by	0.540	,,
the fourth day by	0.240	,,
Total increase	2.300	grammes

So that the fruits gave off 2.3 grammes or 0.44 $^0/_0$ of carbonic acid in four days.

The chemical changes taking place during the after-ripening process were now studied. Each day a banana was broken off from a green unripe bunch of the fruit and when doing this care was taken to select the specimen from the same row of the bunch from which the previous one had been taken and thus to obtain samples of the same initial ripeness. The fruit was first peeled and rubbed to pulp in a mortar. I determined the amount of moisture by drying 10 grammes to a constant weight. Next 100 grammes of the pulp were extracted with alcohol and the residue dried and weighed. I evaporated the alcoholic solution after addition of a little calcium carbonate with the object of neutralising the acids. The residue was dissolved in water, additioned with a little solution of neutral lead acetate and made up with water to 100 cM^3 in order to get the sugars in the solution in the same concentration as that in which they originally were present in the pulp. I determined polarisation and reducing sugar in this solution both before and after inversion and calculated from the figures obtained the amount of sucrose, glucose and fructose after having stated that no other sugars were present in the liquid.

I pulverised the dried residue left behind after the alcoholic extraction of the pulp and extracted part of it with cold water. This extract was evaporated to a small volume and precipitated with alcohol. The precipitate was collected on a weighed, ashless filter washed with alcohol, dried, weighed, incinerated and the loss of weight occasioned by the combustion of organic matter was recorded as dextrin after I had convinced myself by the red coloration which iodine solution produced in the solution of such a precipitate that it really was dextrin.

A second portion of the residue was hydrolysed with hydrochloric acid under pressure and the amount of glucose thus obtained calculated as starch. Finally, I determined the percentage of nitrogen and calculated from this figure the amount of albuminoids by multiplication with the factor 6,25. The figures for the different analyses follow here:

Date of the analysis	17th April	19th April	20th April	22d April	23d April	24th April
Degree of maturity	Unripe the skin adheres to the fruit	Unripe the skin loosens	Begins to ripen	Alm. ripe	Ripe	Over-ripe
% Skin	45	44	43	39	37.8	36.2
% Fleshy matter	55	56	57	61	62.2	63.8
Composition of the pulp						
Moisture	58.24	59.21	59.48	59.86	60.88	61.12
Dry substance	41.76	40.79	40.52	40.14	39.02	38.88
Insoluble in alcohol	39.41	34.06	29.58	20.98	15.30	13.00
Soluble in alcohol	2.35	6.73	10.94	19.16	23.72	25.88
Sucrose	0.86	4.43	6.52	10.50	13.68	10.36
Glucose	0.25	0.96	1.80	3.18	4.72	6.4
Fructose		0.90	1.53	2.70	3.61	4.8
Dextrin	trace	0.52	0.59	0.60	0.65	0.65
Starch	30.98	24.98	20.52	13.8[illegible]	9.59	7.68
Albuminoids	2.65	2.60	2.60	2.58	2.58	2.55
Ash	0.94	0.96	0.97	0.95	1.00	1.01

The skin contains much rubber, fibre and also a small amount of soluble carbohydrate and its composition calculated in 100 parts of dry substance does not vary considerably in the green and in the ripe state. The water content, however, diminished greatly during ripening so that the shrinkage of the skin is chiefly due to loss of water.

The analysis of the pulp shows large differences during the after-ripening because of the starch being rather suddenly transformed on a large scale into sucrose.

That the sugar present in the ripe fruit was really sucrose was proved by evaporating to a small volume the clarified alcoholic extract from fully ripe bananas and allowing it to crystallise. After some time it deposited crystals which were recognised to be sucrose by numerous chemical and physical tests. In the ripe fruits this sucrose becomes partly inverted or consumed by the aspiration either as such or as products of its inversion. The latter possibility is the more probable one, as, first of all, much carbonic acid is formed during the after-ripening and secondly because the fructose is in every case present in a smaller proportion than the glucose. It is evident, therefore that these two constituents are not consumed together as sucrose, but separately after the splitting up of that body and then the fructose more readily so than the glucose.

During the saccharification process a little dextrin is formed too.

b. Mango (Mangifera).

The mango fruit, as a rule, is picked when still unripe; in this state the fruits are internally white, hard, acid and flavourless, but within a few days they undergo an after-ripening process which renders them tender, full-flavoured, and yellow or orange-coloured.

This period is, as in the former case, soon followed by over-ripeness and decay.

A few mango fruits, of a variety which bears very sweet and well-flavoured fruits when ripe, were picked green, placed on a cool spot at a temperature of 28° C. and weighed every day with this result

N⁰.	29th Sept.	1st October	2d October	4th October
I	247 Gr.	243 Gr.	241 Gr.	240 Gr.
II	229	226	224	223
III	227	223	222	219.5
IV	249	247	246	244

Five green mangos were weighed and placed under a glass bell jar, through which a current of air free from carbonic acid was conducted which afterwards was made to pass through a Liebig potash bulb.

This latter was weighed daily and the 5 fruits only after the end of the experiment.

The 5 fruits weighed originally	1139.3 grammes
After 3 days	1121.3 ,,
and therefore lost in 3 days	18.0 grammes

The potash bulb increased during

the first day by	1.712 grammes
the second day by	1.276 ,,
the third day by	1.570 ,,
Or in three days	4.558 grammes

The fruits gave off 4.558 grammes or $0.40^{\circ}/_{0}$ of carbonic acid in three days.

Just as in the case of bananas a mango fruit from a parcel having practically the same initial maturity was daily analysed; and this time the analysis extended with a determination of free and total citric acid. I had previously stated that the acid in the mango really was citric acid and that no other organic acid could be found in it.

I determined the free citric acid by titration with 1/10 normal potash in the boiled fruit whilst the amount of total citric acid was determined by extracting the boiled fruit with alcohol and precipitating the citric acid in the alcoholic liquid by means of barium acetate. The precipitate was filtered off, washed, incinerated and finally, I determined the carbonic acid in the ash which was of course equivalent to the total citrate in the precipitate. The figures obtained follow here.

The yellow colouring matter, which is produced during the ripening process, shows the same reactions as the carotine from carrots, the same spectroscopic appearance and in fact resembles it in every respect.

During the after-ripening the starch is transformed into sucrose, which later on becomes hydrolysed and splits up into glucose and fructose. In the beginning of the process the fruit liberates water but this constituent increases afterwards owing to the combustion of the carbohydrates. The citric acid is vigorously attacked and the decrease in the acid taste during the after-ripening is not due to an increase

Date of the analysis	29th Sept.	1st October	2d October	4th October
Degree of maturity	Unripe	Almost ripe	Ripe	Over ripe
Moisture	83.34	82.95	81.95	83.20
Dry substance	16.66	17.05	18.05	16.80
Soluble in alcohol	6.36	15.18	15.54	14.70
Insoluble in alcohol	10.30	1.87	2.51	2.10
Sucrose	2.57	10.50	12.27	9.31
Glucose	0 60	1.53	1.30	2.10
Fructose	1.90	2.10	2.01	2 60
Starch	8.53	0.55	0	0
Free citric acid	1.36	0.34	0.25	0.10
Total citric acid	1.31	0.37	0 21	0.10
Ash	0.42	0.44	0.41	0.43
Albuminoids	0.80	0.80	0.75	0.73

in the sugar content, nor to a neutralisation of the acid but solely to combustion and thus destruction of the organic acid itself.

C. *Tamarind* (*Tamarindus*).

The tamarind fruits remain on the tree untill they are fully ripe and thus do not undergo any after-ripening process after being plucked or shaken off. In the unripe state the flesh is white and hard and fills the whole pod so that the woody skin is firmly attached to it. Later on, when the fruit ripens, the flesh becomes tender and brown and owing to evaporation, shrinks in such a way that a large empty space exists between the dry pulp and the hard skin. The composition of the pulp of tamarind fruits in several stages of ripeness is given here. (see p. 80).

In this case too the starch has become transformed into sugar, during the ripening but this time not into sucrose, but into a mixture of glucose and fructose. At the same time a great deal of water was evaporated, causing the fruit to shrink in its envelope and finally much acid was consumed by respiration, since the amount of total tartaric acid in the dessicated fruit was smaller than that in the so much more juicy one of a month before. The increase of the percentage sugar after the period of maturity is due to the

Date of the analysis	11th May	27th May	20th June	15th July
Degree of maturity	Green	Almost ripe	Ripe	Dessicated
Dry substance	15.86	38 46	40 92	76.20
Moisture	84.14	61.54	59.08	33.80
Glucose	0.40	10.10	20.4	25.10
Fructose	0.33	5.10	11.6	10.6
Fibre and pectin	3.27	8.10	7.90	14.57
Starch	3.33	1.25	0	0
Free tartaric acid	3 25	15.8	14.6	—
Total tartaric acid	4.85	18.1	16 4	14.4
Potassium bitartrate.	4.00	5.76	4.50	—

strong concentration by evaporation, because no fresh formation of sugar can possibly have taken place in so dry a fruit.

d. Sapodilla (Achras sapota)

The fruits are plucked tree-ripe; in which state they are green and hard, and contain tannin and gutta-percha dissolved in the sap, which render the fruit unfit for eating. After they have been preserved in bran, the gutta-percha as well as the tannin, become insoluble and the fruit itself gets tender, full-flavoured and palatable. On examining sections of the fruit one sees the coagulated gutta-percha as a series of white strings, while the tannin is deposited as insoluble matter in some cells.

The analyses of such fruit in a tree-ripe and full-ripe condition are given here.

	Tree-ripe	Full ripe
Moisture	74.76	75.20
Dry substance	25.24	24.80
Sucrose	7.80	7.02
Glucose	2.85	3.7
Fructose	2.70	3.4
Starch	Absent	Absent
Pectine	3.34	4.00
Albuminoids	0.45	0.40
Ash	1.50	1.50

Unlike the after-ripening of the former three fruits, this one is not due to saccharification of starch. The amount of sugar before and after the full ripening is the same, but in this case the fruit has become palatable by the softening of the hard pectin and by the deposit of tannin and gutta-percha from the juice as insoluble bodies.

I have to mention here that I did not find lactose in this fruit which has been stated by BOUCHARDAT as being one of its constituents. They, however, contain much pectin and owing to the presence of this body the juice yielded a fair amount of mucic acid on oxidation with nitric acid; this renders the supposition probable that this acid, considered by BOUCHARDAT as an evidence of the presence of lactose, has simply come from the pectin.

II. Agents of the saccharification during after-ripening.

When studying the fruits which come first into account in the research under consideration, viz. the banana and the mango fruit, we found in a certain stage of the development a rather sudden transformation of starch into sucrose, followed in a later stage by inversion and partial transpiration of the products of inversion. From experiments on the determination of the carbonic acid in the atmosphere in which this sudden transformation took place, I came to the conclusion that just the period of the rapid saccharification coïncided with a strong development of carbonic acid, or with a powerful oxidation and degradation. At the same time the moisture on the inside of the glass bell jar in which the fruits ripened showed that a copious evaporation had accompanied the oxidation.

The figures for the carbonic acid from the bananas showed on the second day a strong development which decreased very soon, whilst those for the mangos remained somewhat stationary for the three days under observation. These data correspond very well with the more rapid after-ripening of the former fruits during this experiment in which they turned from green into yellow even on the second day.

The transformation is therefore accompanied by oxidation and I tried to check it by excluding the fruits from the free access of oxygen. To this end I covered a few green mango and banana fruits with collodion and kept them together with a few similar fruits not covered with an impermeable layer. The fruits covered with collodion did not ripen well, and were converted into decayed masses, while locally the wrinkles occasioned by the dying off of the fruit caused the collodion layer to burst and thus made the experiment unreliable. Moreover it might well be that the decay was not only to be ascribed to the exclusion of oxygen but to the hindered evaporation which would be injurious to the fruit.

In order to elucidate this point, a few bananas were placed in a tube, through which a current of nitrogen passed, while at the same time some other bananas from the same part of the bunch were kept in the ordinary atmosphere. When the latter had become yellow, tender and ripe, those in the nitrogen tube had still retained their green appearance. The analyses of the peeled fruits of the two parcels yielded these figures.

	In nitrogen	In air.
Moisture	70.54	68.36
Insoluble in alcohol.	25.90	11.06
Soluble in alcohol.	3.57	20.58
Sucrose	0.31	13.66
Reducing sugars	0.94	4.80

It followed then, that the after-ripening in the air had gone on uninterruptedly whilst the fruits kept in the nitrogen atmosphere had remained unchanged and had preserved their starch content; so that free access of oxygen is an indispensable condition for the saccharification of starch in the fruit.

The following experiments were undertaken with a view to ascertaining whether this saccharification was brought about by a vital process or by the action of some diastatic ferment present in the fruit.

A jelly consisting of isinglas and agar agar of such a composition that it was solid at the ordinary temperature was mixed with 1% of starch, poured into a series of Petri dishes and sterilised. Slices of green mango and banana fruit or pieces of half ripe tamarind fruit were placed on the stiff jelly in some dishes and on that of others figures and letters were traced with a pencil dipped in mango-juice. After two, or sometimes more, days the particles of fruit were removed and the jelly covered with a very dilute solution of iodine in potassium iodide which after having remained there for a minute was washed off. In every case not only the spot where the fruit had been placed or where the pencil strokes had been applied, remained white, but all round a white stain spread out, lined with a red border which gradually faded into the surrounding blue coloration of the still unattacked starch. The longer the dishes had been allowed to stand, the larger was the white stain. In every one of these cases, therefore, a diastatic ferment had diffused from the fruits and from the juice, which had transformed all the starch, it could get hold of through the state of dextrin into sugar.

When the iodine solution was allowed to act too long on the jelly, the iodine penetrated through the surface layer and reached the lower one, where the starch was still unattacked, thus colouring the whole dish blue. Finally pieces of banana and tamarind fruit were placed on slices of sterilised potato; the result was that the saccharification of the starch caused more or less deep cavities to appear in the places where the fruits had been applied.

All this however is not yet a direct proof that the saccharification has been occasioned by a ferment; and in order to make this clear I immersed slices of banana into alcohol, left them there during a couple of days, then took them out, expelled the alcohol by means of a current of sterilised air and placed them again in Petri dishes on a layer of starch emulsion stiffened with isinglass and agar agar. Though not so rapid as in the case of the much more juicy fresh fruit, yet also here the ferment diffused through and after the application of the iodine solution the white stains with the red borders became visible.

A quantity of mango juice was added to a boiled and re-cooled solution of 3°/₀ starch at 50° C. and kept at that temperature for some time. The liquid, which, at the outset, had given a deep blue reaction with iodine solution only became red when at the end of the experiment this test was repeated; this coloration did not undergo any change even if the mixture was kept for some time longer or if a fresh quantity of mango juice was added. The total amount of sugar, contained in the liquid (for the mango juice itself had also contained sugar) was higher after the reaction than before, which showed that the mango juice had contained a diastatic body with power to transform starch into dextrin and into sugar.

Now the question still remained which sugar is formed in the laboratory outside of the living organism.

The ripening fruits and their juices already contain so much sugar, which mixes with the small amount of sugar formed by the saccharification of the starch that the proper identification of that latter portion is extremely difficult if not impossible.

In order to eliminate the influence of the already existing sugar, ripening banana fruits were peeled and repeatedly triturated with alcohol and the extracted pulp, which contained as little sugar as possible was pressed and brought into glycerin. After a few days the amount of sugar and its nature was ascertained in the glycerin by polarimetric and copper tests both before and after inversion. Next 100 grammes of this glycerin were mixed with a 3 °/₀ starch solution, warmed to 40° C. and kept at that temperature for a couple of hours. After that the dissolved starch and dextrin was precipitated with alcohol, filtered, a pinch of calcium carbonate was added to the filtrate to prevent inversion by the slightly acid reaction of the filtrate, and the alcohol was evaporated off. The syrupy residue was dissolved in water, diluted to the volume of 100 cM.^{3} and used for the determination of the sugars by the polarimeter and Fehlings solution before and after inversion.

The original glycerin solution had contained 0.17°/₀ of glucose both before and after inversion, while after the treatment with starch 100 grammes of the solution contained 0.60 grammes of reducing sugars before inversion and 0.67 after that operation, which shows that 0.43 grammes of glucose and 0.07 grammes of sucrose (?) have been formed from the starch by the ferment. The polarisation of the solution was $+ 0.9$ before and $+ 0.4$ after inversion, giving evidence, that notwithstanding the precipitation with alcohol, a small amount of starch or dextrin has still remained dissolved.

At any rate from the fact that the exclusion of oxygen prevents the saccharification of the starch in the fruit and from the negative results of the experiments on formation of sucrose by means of fresh juice and of the precipitated and re-dissolved ferments, it follows that the rapid transformation of starch into sucrose during the after-ripening of some fruits is a vital process and not a consequence of the action of some ferment contained in the fruit which, just as diastase forms maltose from starch, could be isolated to form large quantities of sucrose from any kind of starch in the laboratory.

Mathematics. — "*Congruences of twisted curves in connection with a cubic transformation.*" By Prof. JAN DE VRIES.

(Communicated in the meeting of May 30, 1908).

§ 1. If x_1, x_2, x_3, x_4 are the coordinates of a point X with respect to a tetrahedron having O_1, O_2, O_3, O_4 as vertices, then

$$x_1 x'_1 = x_2 x'_2 = x_3 x'_3 = x_4 x'_4$$

determines a cubic transformation which transforms the right line

$$x_k = \lambda a_k + \mu b_k$$

into a twisted curve ω^3, represented by

$$\rho x'_k = \frac{1}{\lambda a_k + \mu b_k}.$$

The congruence Γ of the curves ω^3 through the five points

O_k $(k = 1, 2, 3, 4, 5)$ is now transformed into a sheaf of rays having as vertex the point O'_5 conjugate to O_5.

To the bisecant b' through O'_5 of the curve σ'^3 brought arbitrarily through O_1, O_2, O_3, O_4 corresponds a β^3 through O_1, O_2, O_3, O_4, O_5, having the right line s as chord.

The following will show that the indicated transformation enables us to deduce by a simple method a number of well-known properties of systems of curves ω^3.

§ 2. Let us consider the curves ω^3 of the congruence Γ cutting the right lines l and m. They are transformed into the right lines through O'_5, resting on two curves λ'^3 and μ'^3. Now the cubic cones, projecting these curves out of O'_5 have besides the right lines $O'_5 O_k$ $(k = 1, 2, 3, 4)$ five edges more in common, which are the images of as many twisted curves belonging to Γ.

From this is evident that the curves of Γ cutting a given right line l form a *surface* Λ^5 *of order five.*

The image of Λ^5 is a cubic cone, projecting λ'^3 out of O'_5 and having the bisecant b' out of O'_5 as nodal edge. Therefore the curve β^3 of Γ having l as bisecant is a *nodal curve* of Λ^5.

If we bring the right line m through O_1 its image is a right line m' passing likewise through O_1 and having therefore with the above mentioned projecting cone of λ'^3 besides O_1 two points in common. From this we conclude that Λ^5 has *five threefold points* O_k.

So the section of Λ^5 with $O_k O_l O_m$ consists of the right lines $O_k O_l$, $O_l O_m$, $O_m O_k$ and a conic through O_k, O_l, O_m cutting $O_p O_q$ and forming with this right line a cubic curve of Γ. Consequently *eleven right lines and ten conics* lie on Λ^5.

§ 3. The curves ϱ^3 of Γ touching a given plane φ, are transformed by the correspondence into tangents t' through O'_5 of a cubic surface Φ'^3 having conic points in O_k $(k = 1, 2, 3, 4)$. The polar surface of O'^5 passes through the four double points O, so it has as image a quadratic surface through those points. The section of the latter with φ is the image of the locus of the points, in which Φ'^3 is touched by the right lines t'. *This conic* contains therefore the points in which φ is *touched* by the curves ϱ^3.

Through O'_5 pass six principal tangents of Φ'^3, the congruence Γ contains therefore *six* curves, *osculating* φ.

The enveloping cone φ'^6 out of O'_5 to Φ'^3 has four nodal edges $O'_5 O_k$; for a plane through $O'_5 O_k$ cuts Φ'^3 according to a cubic curve with node O_k, sending but four tangents through O'_5, so that in that plane $O'_5 O_k$ replaces two edges of the cone.

So φ'^6 has with an arbitrary cubic curve through the four points O_k ten points in common lying outside O_k. By applying our transformation we find from this that the curves of Γ touching φ form *a surface* Φ^{10} *of order ten.*

A right line through O_1 cuts φ'^6 in four more points; on its image therefore rest four curves ϱ^3 touching φ. From this ensues that Φ^{10} has *five sixfold points* O_k.

The right lines $O_k O_l$ lie therefore on Φ^{10}; it can as follows become evident that they are *nodal rightlines.* A right line resting on $O_1 O_2$ and $O_3 O_4$ has six points in common with φ'^6. So its image must have on $O_1 O_2$ and $O_3 O_4$ four points in common with Φ^{10}.

The section of Φ with $O_1 O_2 O_3$ consists of the right lines $O_1 O_2$, $O_2 O_3$, $O_3 O_1$ to be counted double and a curve of order four, having nodes in O_1, O_2, O_3 and in the point of intersection of the nodal line $O_4 O_5$; thus it consists of two conics. These conics form evidently with $O_4 O_5$ two cubic curves of Γ, touching φ.

Consequently there lie on Φ^{10} ten *nodal lines and twenty conics.*

When we regard the tangential cones out of O'_5 to two quadrinodal cubic surfaces Φ'^3 it follows readily that Γ contains *twenty* curves touching two given planes.

§ 4. To determine how many curves ϱ^3 can be brought through four points O_k having the right line b as bisecant and resting on the right lines c and d, we have but to find the number of right lines r' which cut β'^3 two times and γ'^3 and δ'^3 one time, when these three curves have four points O_k in common.

Now the chords of β'^3 resting on a right line l' form a biquadratic scroll on which β'^3 is nodal curve, having thus with γ'^3 besides the four points O four more points in common. From this follows immediately that the right lines cutting β'^3 twice and γ'^3 once also form a biquadratic scroll Σ'^4. The cones which project these curves out of a point of β'^3 having two edges in common, not containing one of the points O, the curve β'^3 is also nodal curve on Σ'^4. With δ'^3 this scroll has besides O_k four points in common; so on γ'^3 and δ'^3 rest four chords of β'^3, and by applying the transformation we find that the curves ϱ^3 which cut b twice and c once form a *surface* Σ^4 *of order four.*

If we bring d through O_1, then its image d' has with Σ'^4 two more points in common; consequently d cuts the surface Σ^4 in two points lying outside O_1, so that O_1 is a node. Therefore the surface Σ^4 has *four double points* O_k.

Evidently b is nodal right line of Σ^4; for, b is the image of the nodal curve β'^3 lying on Σ'^4.

Through a point S of b pass two curves ϱ^3; their two points of intersection S' and S'' with b are the points which b has still in common with the surface A^4 determined by c, S and the points O.

As the pairs of points S and S' form a (2,2) correspondence, *four* curves ϱ^3 can be brought through four points, which *touch* a right line and *intersect* an other right line.

The section of Σ^4 with the plane $O_1 O_2 O_3$ has nodes in O_1, O_2, O_3 and in the intersection with b; so it consists of two conics. One of these conics contains also the intersection of c; it is completed to a degenerated ϱ^3 by the right line out of O_4 resting upon it and upon b. The second conic contains the intersection of the transversal drawn out of O_4 to b and c and forms with this right line a ϱ^3.

On the surface Σ^4 lie therefore *eight conics, nine simple right lines and a nodal line.*

§ 5. The number of curves ϱ^3 through O_k $(k = 1, 2, 3, 4)$ resting on the right lines a, b, c, d is evidently as large as the number of transversals of four cubic curves $\alpha^3, \beta^3, \gamma^3, \delta^3$ brought through O_k. The scroll (α, β, l), having α^3, β^3 and a right line l as directrices, is of order 14, l being fivefold and each plane through l containing nine right lines. If l_0 passes through O_1 a plane through l_0 contains but four right lines, so that the order of the scroll (α, β, l_0) amounts but to 9. From this ensues that (α, β, l) possesses four twofold points O_k.

With γ^3 the scroll (α, β, l) has 22 points in common outside O_k; so (α, β, γ) is of order 22.

On the scroll (α, β, l_0) we find that O_1 is fivefold, because a right line through O_1 cuts four generatrices; on the other hand O_2, O_3 and O_4 are threefold points, for a right line through O_2 cutting the fivefold right line l_0, meets but *one* generatrix more. With γ^3 the scroll (α, β, l_0) has still $9 \times 3 - 5 - 3 \times 3 = 13$ points in common besides the multiple points. In connection with the above follows from this that O_1 is a ninefold point on (α, β, γ).

Of the points of intersection of (α, β, γ) with δ^3 36 lie in O_k; consequently $\alpha^3, \beta^3, \gamma^3, \delta^3$ have thirty common transversals.

Therefore we can bring through *four* points *thirty* cubic curves resting on *four* given right lines.

§ 6. Let us now consider the surface ψ^{30} formed by the curves ϱ^3 resting on a, b and c. Through a point A of a and the points O

pass five ϱ^3 cutting b and c. From this is evident that a, b and c are *fivefold right lines.*

With a right line m through O_k the scroll (α, β, γ) has thirteen points lying in O_k in common, so its image m' (right line through O_k) cuts ψ^{30} likewise in 13 points lying outside O_k. We conclude from this that the four points O are seventeenfold on ψ^{30}.

So the right lines $O_k O_l$ lie on this surface; that they are fourfold right lines can be shown in this manner.

As O_k and O_l are ninefold on (α, β, γ) the right line $O_k O_l$ is cut outside those points by $22-18=4$ transversals of the curves α, β, γ; the images of these right lines are conics through O_k and O_l resting on $O_m O_n$, b, c and d and forming with $O_m O_n$ a ϱ^3 of the system.

The section of ψ^{30} with $O_1\, O_2\, O_3$ can consist outside the three fourfold right lines only of conics; these are easy to indicate. In the first place we can bring through O_1, O_2, O_3 a conic cutting b and c; it is completed to a ϱ^3 by each of the two right lines out of O_4 resting on the conic and on d. Then the sections of d and of the transversal with O_4 to b and c with O_1, O_2, O_3 determine a conic forming with the indicated transversal a ϱ^3. So we have in O_1, O_2, O_3 three double and three simple conics; with the three fourfold right lines they form a section of order 30.

On ψ^{30} lie therefore 4 seventeenfold points, 3 fivefold, 6 fourfold and 36 simple right lines, 12 double conics and 36 simple conics.

Astronomy. — "*Contributions to the determination of geographical positions on the West coast of Africa. III.*" By C. SANDERS. (Communicated by E. F. VAN DE SANDE BAKHUYZEN).

(Communicated in the meeting of May 30, 1908).

I. Introduction.

After a stay in Europe during the winter 1902—1903 I returned to Portuguese West Africa and remained there until the autumn 1906 when I again went to Europe for some time.

During this period 1903—1906 I have once more tried to contribute to the determination of geographical positions in these parts as much as time and circumstances allowed. Circumstances, however, were often unfavourable to my observations, and hence the results obtained are less than I had desired and expected at first.

The results obtained may be ranged under three heads.

1. *New determinations at Chiloango.* In November and December

1903 I made here a new series of determinations of latitude by means of zenith distances in the meridian. But I did not succeed in securing new data with which to correct the determination of the longitude, and at last I have entirely given up this plan, until I should possess a telescope of the required dimensions for the observation of occultations of stars[1]), because the observations of the latter will certainly lead to a greater accuracy in the determination of the longitude than can be attained by means of lunar altitudes with my relatively small instrument.

2. *Determinations of astronomical coordinates at different stations in the Chiloango district.* On two journeys, one to N'Kutu on the upper course of the Chiloangoriver from 22 to 31 December 1903 and a longer journey through Mayombe[2]) in June 1904, I was able to make determinations of latitude and longitude. The reason why these could not be made oftener lies chiefly in the peculiar difficulties attached to the transportation of the instruments especially of the chronometers. The best way of transporting them is by water by means of a canoe, and even then one must constantly pay attention to avoid shocks caused by trees floating down the river. When the chronometers had to be transported by land, I used a hammock suspended from a long stick carried by two negroes; while mounting hills they tried to keep the stick as much horizontal as possible.

Another circumstance which makes it difficult to obtain accurate results is that these excursions can be undertaken only during the dry season, when the nightly sky is as a rule overcast, so that one must take recourse to observations of the sun, and lastly in many parts one meets with great difficulties in finding a proper dwelling place, because prosperous negro villages, which formerly existed, are almost entirely depopulated and turned into desert in consequence of the trypanosomosis, which has raged there.

On my journey in December 1903 the instruments were entirely transported by water, first by steamer to Mayili then by canoe to N'Kutu. At this latter station I secured determinations of latitude and longitude.

The journey through Mayombe in June 1904 also began by steaming up the Chiloango- (or Loango-) river to Mayili. We there arrived on June 2 and I made a time determination in order to control the longitude determined previously. We then travelled by land to

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[1]) I received for some time past (1907) a telescope of Zeiss of 80 mm. aperture and 120 cm. focal length, with which I have already made some experiments.

[2]) The name of a part of the Chiloango district.

Chimbete (June 3) and then per canoe up the river to N'Kutu. The first transport by land, when the carriers were not yet accustomed to their uncommon task, unfortunately caused a perturbation in at least one of the two chronometers, which appeared from the comparisons between them.

Also at N'Kutu I made a time determination on June 5, in order to obtain another result for the longitude of that place. On June 6 we continued our journey by land often along very difficult roads through woods and over hills and some times across small streams. We first went to the north east as far as N'Vyellele, a village 28.5 kilometers north east of N'Kutu (June 7), and then we travelled to the west during three days until June 10, when we reached Buku-Zan, a village on the Luali, a tributary river of the Loango.

On June 13 and 14 we made an excursion from Buku-Zan to the north to M'Pene Kakata, but the rest of the time until June 16 I stayed in the former place and availed myself of this opportunity to determine its longitude and latitude.

On June 16 we returned from Buku-Zan to N'Kutu. This time we went directly to the south east, and after we had covered a distance of 38 kilometers we arrived at N'Kutu on June 17. Thence we returned by the way we had come via Chimbete and Mayili to Chiloango (18—23 June). In the mean time I secured determinations of latitude and longitude at Chimbete.

3. *Connection of a great number of secondary points with the astronomically determined stations, by means of compass directions and distances.* It was my intention to form by means of my astronomical determinations a net of primary points with which I might connect a great number of intermediate points whose relative positions I had determined on many journeys by means of compass directions and distances, in order thus to reach also for the latter a satisfactory accuracy. In this I have partly succeeded, but for the southern part of the district it is still necessary to make the astronomical determination of one and if possible 2 stations on the Lukula river, Chipondi and perhaps Pouro, the more so as the preliminary result of my secondary determination of the station Lemba on this river differs much from that which Mr. CABRA had obtained some years ago, when he determined the demarcation between the Freestate and Portuguese Congo.

I shall try to fill up this gap. But the difficulties are especially great in these parts, as the trypanosomosis has badly raged here of late. At any rate it will be desirable to put off till later the communication of my secondary determinations.

CORRECTIONS AND RATES OF THE CHRONOMETERS.

Date	M. T.	Temp. C.	Chron. Hewitt			Chron. Hohwü	
			Corr.	D. Rate	D. Rate 20° C.	Corr.	D. Rate
	h		m s	s	s	m s	s
1903 May 15	8.12		+47 59.03			+46 55.03	
„ 20	8.15	24.5	58.38	—0.13	–1.25	56.38	+0.27
„ 25	8.46	24.0	57.24	—0.23	–1.23	57.24	+0.17
June 20	8.18	22.0	38.13	—0.74	–1.24	48.13	—0.35
„ 27	8.10	19.6	31.41	—0.96	—0.86	45.41	—0.39
July 3	8.32	19.6	26.06	—0.89	–0.79	40.06	—0.89
„ 10	8.25	19.7	18.71	–1.05	—0.97	32.71	–1.05
„ 17	8.10	20.1	11.17	—1.08	—1.10	27.57	—0.73
„ 25	8.50	19.1	1.98	—1.15	—0.93	20.48	—0.89
Aug. 4	8.15	9.7	+46 51.06	—1.09	–1.01	15.06	—0.54
„ 24	8.22	21.0	41.03	—0.50	– 0.52	8.53	—0.33
Oct. 12	8.45	24.4	41.88	+0.02	–1.08	13.38	+0.10
„ 19	8.10	25.6	44.45	+0.37	–1.03	17.95	+0.65
Nov. 5	7.93	25.5	54.35	+0.58	—0.80	21.85	+0.23
„ 16	8.53	26.0	+47 2.31	+0.72	—0.78	22.81	+0.09
„ 20	7.98	25.6	4.32	+0.50	—0.90	23.92	+0.28
Dec. 20	8.05	25.3	17.97	+0.46	—0.86	48.97	+0.83
1904 Jan. 3	8.04		28.08	+0.72		52.08	+0.22
„ 6	8.43	25.3	28.70	+0.21	–1.11	53.20	+0.37
„ 17	7.97	25.7	35.56	+0.62	—0.80	+47 0.56	+0.67
„ 22	8.20	25.4	37.35	+0.36	—0.99	5.35	+0.96
„ 29	8.44	25.2	40.79	+0.49	– 0.81	10.79	+0.78
Febr. 9	8.40	25.3	45.93	+0.47	—0.85	19.43	+0.78
„ 20	8.05	25.8	55.41	+0.86	—0.59	21.41	+0.18
March 4	8.23	25.8	+48 8.69	+1.02	–0.43	30.69	+0.71
„ 31	8.08	25.7	38.47	+1.10	—0.32	43.47	+0.47
May 12	8.08	25.5	+49 13.51	+0.83	—0.55	+48 8.01	+0.58
„ 23	7.80	24.5	14.83	+0.12	—1.00	18.33	+0.94
„ 30	8.37	24.4	15.66	+0.11	—0.99	26.66	+1.18
June 24	7.70		22.83	+0.29		47.33•	+0.83
Aug. 1	8.30	20.9	17.42	—0.14	– 0.36	+49 8.92	+0.57
Sept. 30	7.90	21.2	+48 58.86	—0.31	—0.61	20.86	+0.20
Oct. 14	8.24	23.8	+49 1.48	+0.19	–0.79	25.98	+0.37

Date		M. T.	Temp. C.	Chron. Hewitt			Chron. Hohwü	
				Corr.	D. Rate	D. Rate 20° C.	Corr.	D. Rate
		h		m s	s	s	m s	s
1904 Oct.	24	8 30	24.3	+49 5 35	+0 39	—0 69	+49 33 85	+0 79
Nov.	5	8.25	24.6	10.03	+0.39	—0.76	42.03	+0.68
„	10	8.25	25.1	11.93	+0.38	—0.90	44.93	+0.58
„	18	8.07	25.1	15.25	+0.42	—0.86	51.75	+0.85
„	29	7.99	25.5	19.97	+0.43	—0.95	+50 3.97	+1.11
Dec.	9	8.10	25.1	26.46	+0.65	—0.63	11.96	+0.80
„	19	8.32	25.0	28.54	+0.21	—1 03	22.04	+1.11
1905 Jan.	2	8.12	24.6	31.26	+0.19	—0.96	34.26	+0.87
„	14	8.10	25.7	36.40	+0.43	—1.01	46.40	+1.01
„	21	9.24	25.6	38.64	+0.32	—1.08	52.14	+0.82
Febr.	12	8.43	25.9	49.17	+0.48	—0.99	+51 2.17	+0.46
„	25	8.54	26.2	57.37	+0.63	—0.91	7.87	+0.44
March	5	8.03	26.4	+50 2.23	+0.61	—1.00	6.73	—0.14
„	25	7.94	26.6	16.72	+0.72	—0.92	10.72	+0.20
Apr.	21	8.22	26.6	36.74	+0.74	—0.90	1.24	—0.35
June	27	8.20	24.1	50.70	+0.21	—0.82	+50 57.70	—0.05
Sept.	1	8.66	21.0	29.38	—0.32	—0.57	29.38	—0.43
„	3	8.64	22.6	29.36	—0.01	—0.65	28.86	—0.26
„	7	8.35	22.6	28.35	—0.25	—0.90	24.35	—1.13
Oct.	19	8.05	24.0	33.86	+0.13	—0.86	1.86	—0.54
„	31	7.99	25.2	37.20	+0.28	—1.03	+49 53.70	—0.68
Nov.	4	8.32	25.1	40.33	+0.78	—0.50	52.53	—0.29
„	22	8.39	26.1	51.46	+0 62	—0.91	39.96	—0.70
Dec.	6	8.18	26.3	+51 2.09	+0.76	—0.82	31.09	—0.63
„	16	8.20	25.6	9.58	+0.75	—0.65	23.58	—0.75
1906 Jan.	8	8.24	26.2	26.52	+0.74	—0.81	9.02	—0.63
Febr.	24	8.45	26.3	+52 8.84	+0.90	—0.68	+48 11.34	—1.23
March	11	8.37	27.3	26.09	+1.15	—0.67	+47 58.09	—0.88
„	21	8.11	26.7	33.93	+0.78	—0.90	48.43	—0.97
Apr.	3	7.90	26.6	43.32	+0.72	—0.92	35.62	—0.99
May	6	8.45	25.8	58.36	+0.46	—1.00	0.96	—1.05
June	1	8.14	24.2	52.20	—0.24	—1.28	+46 29.84	—1.21
„	18	8.09	22.7	39.07	—0.77	—1.43	1.57	—1.66
July	19	8.62	20.8	8.52	—0.98	—1.22	+45 9.52	—1.68

II. *Time determinations at Chiloango. Corrections and rates of the chronometers.*

In 1903 before I left for Africa I added to my chronometer of Hewitt another of Hohwü. During my stay at Chiloango from May 1903 to July 1906 I have regularly controlled both by making at proper intervals time determinations in the same way as before by altitudes determined with my altazimuth. Moreover I have daily intercompared the two chronometers.

With regard to the time determinations themselves I need only add to what has been said before:

1. that new determinations of the value of a level-part yielded 5″.4, exactly as before;

2. that the flexure and the division errors of the instrument were regularly taken into account according to the formulae in "*Contributions* I".

Here follow the results for the corrections and rates of the chronometers. The rates, and also the temperatures added to them, refer to the interval between the date on one line above and that on the line itself. The temperatures for the periods of the two journeys are wanting. To the "Rates Hewitt 20° C." I shall refer later.

I have first investigated the rates of the chronometers with regard to the temperature and to this end I have formed mean rates for periods of about 2 months, in each summer and winter.

Period	Temp. C.	Chron. Hewitt.		Chron. Hohwü.	
1903 June 20—Aug. 4	19.63	$-1^{s}.05$		$-0^{s}.73$	
Nov. 5—March 31 1)	25.58		$+0^{s}.71$		$+0^{s}.59$
1904 June 24—Sept. 30	21.03	-0.24		$+0.34$	
1905 Febr. 12—April 21	26.42		$+0.70$		-0.01
June 27—Sept. 1	20.95	-0.32		-0.43	
1906 Jan. 8—April 3	26.83		$+0.90$		-1.10
June 18—July 19	20.82	-0.98		-1.68	

For the chronometer of Hewitt I found a very distinct influence of the temperature and, in so far as I could find then, no variation with time.

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1) I have excluded the period of my journey from Dec. 20 to Jan. 3.

For the simple means of the 4 winter and the 3 summer rates and of the temperatures belonging to them I find:

26°.28 $+ 0^s.77$
20 .61 $- 0 .65$

hence: Variation per degree $+ 0^s.25$ ¹)

By means of this coefficient of temperature I have reduced all the rates to 20°; these reduced rates are given in the table above in the column: D. Rate 20° C. The simple mean value of these reduced rates is $- 0^s.87$, from which the real mean reduced rate $- 0^s.83$ differs only little. By forming the differences between the reduced rates and their mean I found for the mean error of a daily rate, disregarding the different lengths of the intervals between the time determinations:

M.E. $\pm 0^s.225$

a very satisfactory result, especially in consideration of the fact that for the whole period of more than 3 years we have adopted a constant rate depending on the temperature only.

For the chronometer of Hohwü the results are somewhat less favourable. One sees at a glance a distinct variation with time which from 1904 seems to continue in the same sense.

In order to derive the coefficient of temperature I have compared each summer rate with the mean of the two neighbouring winter rates and thus found:

Rate summer—winter $+ 0^s.78$
$+ 0 .03$
$- 0 .05$

A regular influence of the temperature does not appear from these data and the greater value of the first difference must be ascribed to an irregular variation in the beginning. Therefore I have accepted for the coefficient of temperature $0^s.00$ and, in order to investigate the variation which is independent of the temperature I have formed mean rates for periods of about three months. They follow here together with the corresponding values for the chronometer of Hewitt reduced to 20°.

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[1] It was impossible to determine also a quadratic term on account of the small differences of temperature. For the years 1901—'02 the temperature coefficient was found to be $+ 0^s.18$.

DAILY RATES FROM PERIODS OF THREE MONTHS.

	D. Rate Hewitt red. to 20°	D. Rate Hohwü
	s	s
1903 May 15—Aug. 4	— 1.08	— 0.49
Aug. 4—Nov. 5	— 0.90	+ 0.07
Nov. 5—Jan. 29	— 0.86	+ 0.65
1904 Jan. 29—May 12	— 0.51	+ 0.55
May 12—Aug. 1	— 0.56	+ 0.72
Aug. 1—Nov. 5	— 0.66	+ 0.34
Nov. 5—Jan. 21	— 0.93	+ 0.91
905 Jan. 21—Apr. 21	— 0.94	+ 0.10
Apr. 21—June 27	— 0.82	— 0.05
June 27—Nov. 4	— 0.72	— 0.50
Nov. 4—Febr. 24	— 0.76	— 0.90
1906 Febr. 24—May 6	— 0.90	— 0.99
May 6—July 19	— 1.29	— 1.51

The values of this table also show the greater regularity of the chronometer of Hewitt for which only the last rate shows a greater deviation. The rate of that of Hohwü seems tolerably constant during the period 1903 Nov. 5—1905 Jan. 21 for which the mean rate amounts to $+ 0^s.61$.

From the differences between the single rates in this period and their mean we find, again disregarding the lengths of the intervals:

M.E. Daily rate Hohwü ± $0^s,30$

still greater than for Hewitt. But on the other hand the large coefficient of temperature of the latter is a disadvantage for periods for which the temperature is not accurately known.

III. New determination of the latitude of Chiloango.

In the months of November and December 1903 I made a new determination of the latitude of Chiloango, again by altitudes observed with my universal instrument, with the only difference that a much greater number of stars was observed, but with only one pointing for each of them at the moment of transit over the meridian. The observations were arranged so that 2 northern and 2 southern stars

1903 DECEMBER 7

Adopted runcorrection for 10′ — 0″.66
„ zenith point 239°59′47″.32
Temperature and barometer for 1st star 25.3 759.4
4th „ 24.9 759.5
6th „ 24.6 759.6
12th „ 24.0 759.8

Star		Readings		Level corr.	Zenithdist.	Refr.	Lat.
		Micr. A	Micr. B				
							—5°11′
α Sculptoris	R	264°40′ 15″	39′ 51″	— 3″89	24°40′ 12″12	25″37	68″01
		15	51				
β Phoenicis	L	197 58 49	58 24	— 2.97	42 1 14.53	49.73	69.94
		48	23				
β Andromedae	R	280 18 7	17 42	0.00	40 18 8.23	46.82	64.95
		7	47				
δ Cassiopeiae	L	175 5 24	5 5	+ 2.59	64 54 31.00	1′ 57.47	65.87
		23	3				
γ Phoenicis	R	278 35 57	35 33	+ 1.08	38 35 58.96	44.13	67.91
		58	33				
α Eridani	L	187 29 33	29 15	— 2.43	52 30 26.79	1 12.04	66.67
		34	11				
γ Persei	R	295 23 16	22 57	— 3.78	55 23 14.28	1 20.03	66.71
		12	56				
ε Cassiopeiae	L	171 38 9	37 56	+ 0.54	68 21 44.73	2 18.50	62.93
		9	55				
α Hydri	R	296 49 0	48 39	+ 0.81	56 49 1.24	1 24.44	65.02
		48 58	35				
γ Andromedae	L	192 56 47	56 23	— 4.86	47 3 18.03	59.55	62.48
		45	22				
α Arietis	R	268 12 3	11 38	— 1.62	28 12 2.27	29.75	59.02
		5	38				
γ Eridani	L	193 15 24	14 55	+ 2.70	46 44 35.38	58.91	64.91
		22	56				

Date	Star		Zenith dist.	Latitude			
				N. R.	N. L.	S. R.	S. L.
1903				— 5°11′			
November 28	ξ Toucani	R	S 60°			57″42	
Zenithp. 180°	α Phoenicis	L	S 38				58″21
	α Cassiop.	R	N 61	66″43			
	γ Cassiop.	L	N 65		71″99		
	α Sculptoris	R	S 25			49.73	
	β Phoenicis	L	S 42				59.27
	β Androm.	R	N 40	65.53			
	υ Piscium	L	N 32		71.42		
	δ Cassiop.	R	N 65	67.73			
	Mean			**66.56**	**71.70**	**53.58**	**58.74**
December 2	γ Cassiop.	L	N 65		67.85		
Zenithp. 210°	α Sculptoris	R	S 25			57.91	
	β Androm.	R	N 40	67.85			
	Mean			**67.85**	**67.85**	**57.91**	
December 6	α Sculptoris	R	S 25			60.98	
Zenithp. 210°	β Phoenicis	L	S 42				64.35
	β Androm.	R	N 40	69.94			
	δ Cassiop.	L	N 65		69.59		
	γ Phoenicis	R	S 39			63.53	
	α Eridani	L	S 53				59.45
	Mean			**69.94**	**69.59**	**62.26**	**61.90**
December 7	α Sculptoris	R	S 25			68.01	
Zenithp. 240°	β Phoenicis	L	S 42				69.94
	β Androm.	R	N 40	64.95			
	δ Cassiop.	L	N 65		65.87		
	γ Phoenicis	R	S 39			67.91	
	α Eridani	L	S 53				66.67
	φ Persei	R	N 55	66.71			
	ε Cassiop.	L	N 68		62.93		

Date	Star		Zenith dist.	Latitude			
				N. R.	N. L.	S. R.	S. L.
					— 5° 11′		
Dec. 7 cont.	α Hydri	R	S 57°			65′′02	
	γ Androm.	L	N 47		62″48		
	α Arietis	R	N 28	59″02			
	φ Eridani	L	S 47				64″91
	Mean		—	**63.56**	**63.76**	**66.98**	**67.17**
December 10	δ Cassiop.	L	N 65		63.11		
Zenithp. 270°	γ Phoenicis	R	S 39			68.08	
	α Eridani	L	S 53				69.66
	φ Persei	R	N 55	61.18			
	ε Cassiop.	L	N 68		64.79		
	α Hydri	R	S 57			68.58	
	β Trianguli	R	N 40	62.54			
	φ Eridani	L	S 47				71.22
	Mean			**61.86**	**63.95**	**68.33**	**70.44**
December 14	γ Phoenicis	R	S 39			62.22	
Zenithp. 300	α Eridani	L	S 53				62.88
	β Arietis	R	N 26	58.41			
	α Hydri	R	S 57			65.99	
	γ Androm.	L	N 47		59.56		
	β Trianguli	R	N 40	64.07			
	φ Eridani	L	S 47				61.99
	δ Hydri	R	S 64			64.13	
	Mean			**61.24**	**59.56**	**64.11**	**62.44**
December 15	δ Cassiop.	L	N 65		68.96		
Zenithp. 330	γ Phoenicis	R	S 39			64.05	
	α Eridani	L	S 53				59.03
	φ Persei	R	N 55	72.49			
	ε Cassiop.	L	N 68		68.16		
	α Hydri	R	S 57			57.46	
	γ Androm.	R	N 47	67.16			
	β Trianguli	L	N 40		68.18		
	φ Eridani	L	S 47				59.67
	Mean			**69.82**	**68.43**	**60.76**	**59.35**

were observed alternately, and of each of these pairs the one in the position circle to the right, the other in the position circle to the left.

The readings were always made with each of the two microscopes both on the preceding and on the following division. The corrections for run and for the level reading were applied exactly as before (comp. *Contrib.* I. p. 280), the refraction was derived from the tables of Bessel and the declinations of the stars were taken as before from the *Nautical Almanac*, i. e. from the catalogue of Newcomb. Only now and then I have also observed stars from the *Berliner Jahrbuch*, namely *v* Piscium, *σ* Cassiopeiae and *φ* Persei. To reduce them to Newcomb I have applied to them the following corrections: — 0″.1, — 0″.8 and + 0″.7, according to data communicated to me by Dr. E. F. v. d. Sande Bakhuyzen.

The reading for the zenith was assumed to be constant for each night and determined so as to make all the stars agree inter se as well as possible. By the regular alternation of the positions of the instrument an error in the adopted zenith point was eliminated almost entirely.

The observations were made in 6 positions of the circle, each differing from the next by 30°.

As an example I will first give the observations of one night in full.

I now proceed to give for all the observations the resulting values for the latitude in 4 columns: for the north stars circle right and left and for the south stars circle right and left. To these I add the approximate zenith distances of the stars.

The observations at zenith point 210° are distributed over two nights, Dec. 2 and Dec. 6. Because it is not permissible to consider the zenith point for the two as exactly equal, it seemed better to exclude from the observations of Dec. 2 the only southern star obtained. For the rest no observations are excluded, not even the few which deviated rather much.

For each position of the circle I have combined the results for the two positions of the instrument, but I kept apart those from the northern and from the southern stars and so I obtained: (see p. 100)

To the results from the northern and the southern stars I have added their differences and their means. In so far as we may assume that the north and the south stars had in the mean the same zenith distance, the former represent the corrections to the measured arcs of 2 z for errors of division + double the correction to the measured z for flexure (comp. *Contrib.* I p. 285), while on the

Zenithpoint	North stars	South stars	N—S	$\frac{N+S}{2}$
	— 5° 11′			— 5° 12′
180°	69″13	56″16	— 12″97	2″64
210	68.81	62.08	— 6.73	5.44
240	63.66	67.08	+ 3.42	5.37
270	62.90	69.38	+ 6.48	6.14
300	60.40	63.28	+ 2.88	1.84
330	69.12	60.06	— 9.06	4.59
Mean	**65.67**	**63.01**	**— 2.66**	**4.34**

same supposition the means from the north and the south stars are free from these two errors.

To derive the errors of division and of flexure we obtain, the mean zenith distance amounting to 49°, with the same notations as before :

$$a' = \quad 2a \sin 98^\circ = -10.''16$$
$$b' = -2b \sin 98^\circ = +\ 0.83$$
$$c' = \quad 2c \sin 49^\circ = -\ 2.66$$

whence, if a stands again for the circle reading:

Correction for division errors to the circle reading $-5.''13 \sin 2a - 0.''41 \cos 2a$

$$= +5.''15 \sin (2a - 175.^\circ 4)$$

Correction for flexure to the zenith distance $-1.''76 \sin z$.

The mean of the values in the last column is:

$$\varphi = -5^\circ 12' 4''.34.$$

The formula for the correction for division errors agrees very well with that derived from the observations of 1900—01, which is of importance for the correction of my other observations of zenith distances. For the coefficient of the flexure I had formerly found —0.″60; the difference may still be ascribed to accidental causes.

Finally I give here the 12 separate results for the latitude, each corrected for division errors and flexure. (see p. 101).

Their mean value must of course be equal to that of the uncorrected results. From the comparison of the former with their mean we derive for the mean error of the final result ± 0.″57. Hence this is:

$$\boldsymbol{\varphi = -5^\circ 12' 4''.34 \pm 0''.57.}$$

	North stars	South stars
	— 5° 12′	
180°	2″72	2″57
210	5.30	5.59
240	5.23	5.51
270	6.65	5.63
300	1.25	2.43
330	4.89	4.29

This result may be combined with that of 1900—01. For the latter I adopt the first value of *Contrib.* I p. (284), but I estimate its mean error to be not less than that which I have now found. Thus:

Latitude of the pier of observation.

1900—01	— 5° 12′ 4″.01 ± 0″.6
1903	4 .34 ± 0 .6
Together	**— 5° 12′ 4″.2 ± 0″.4**

I think that the agreement is quite satisfactory.

IV. *Determinations of the longitude and the latitude of N'Kutu, Mayili, Buku-Zan and Chimbete.*

1. *Journey of* 1903 *December* 22—31. *Observations at N'Kutu.* During this journey the chronometers were transported all the way by water, hence extraordinary perturbations are not to be feared. But the temperature was certainly higher than at the same time at Chiloango; it amounted at least to 26° and may have been between 26° and 30°. A comparison of the rate of Hewitt from Dec. 20 to Jan. 3 with the mean reduced rate for those months would yield a temperature of 26°.4, which is of course an uncertain estimation. Although there is no reason to expect any difference in temperature between the journey to N'Kutu and the journey back, yet the uncertainty about this affords a disadvantage for Hewitt and therefore, for the determination of the longitude, I have finally given equal weights to the two chronometers.

The computation of the time and the latitude at a place of which the geographical position is unknown had of course to be made in successive approximations. Here I shall give only the final results.

The observations were made in the factory of the firm Hatton and Cookson.

Determination of the longitude. A time determination of 26 Dec. by means of 4 observations of β Orionis in both positions of the instrument, each time over 7 horizontal threads, yielded the following corrections of the chronometers to the mean time of N'Kutu. Together with these I give the corrections to the mean time of Chiloango derived by simple interpolation — the best thing to be done — between the time determinations of Dec. 20 and Jan. 3, and finally the resulting difference of longitude.

December 26.296 (M. T. Chiloango).

	Hohwü	Hewitt
Correction to M. T. N'Kutu	$+ 48^m48^s.85$	$+ 49^m22^s.35$
,, ,, ,, Chiloango	46 50 .29	47 22 .27
Difference of longitude	— 1 58 .56	— 1 60 .08

Adopting the simple mean of the two results, we find for the longitude of N'Kutu relatively to Chiloango

$$-1^m\ 59^s.32.$$

Determination of the latitude. On December 29 I secured a determination of the latitude by 3 pairs of observed zenith distances, i.e. three observations in each position of the instrument, of β Andromedae ($z = 40°$ North) and by 2 pairs of α Eridani ($z = 53°$ South).

The results were:

β Andromedae	1st pair	$-4°57'\ 9''.90$
	2d ,,	11.06
	3d ,,	11.24
	Mean	10.73
	Corrected	$-4°57'\ 5''.74$
α Eridani	1st pair	$-4°56'57''.69$
	2nd ,,	59.81
	Mean	58.75
	Corrected	$-4°57'\ 3''.72$

Hence the mean result for the latitude is:

$$\mathbf{-4°\ 57'\ 4''.7}$$

2. *Journey of* 1904 *June* 2—23. *Corrections of the chronometers.*

As this journey was made almost entirely by land the circumstances were much less favourable for the regularity of the chronometers, in spite of all precautions taken. The intercomparisons, which were made at least once every day, clearly show small irregularities now and then and once on June 3, when the carriers were not yet accustomed to their task, as I have said before, a serious perturbation occurred.

The instruments were almost always carried in the shadow of the woods and only a few times they can have been exposed to the sunbeams. We must assume, however, that they were subject to the general fall of temperature which occurs in these parts in June, and thence follows that we may not accept a constant rate for the chronometer of Hewitt.

From my regular thermometer readings in 1903 and 1905 I derive for the mean fall of temperature during June 2°.18, i. e. on an average per day 0°.073; this would cause a variation of rate for Hewitt of $-0^s.018$ per day. On this supposition and starting from the time determinations at Chiloango of May 30 and June 24, the daily rate would have been at the beginning (May 30—31) $+0^s.50$ and at the end (June 23—24) $+0^s.08$.

As the temperature coefficient of Hohwü may be considered zero, we may gather some evidence on this point from the relative rates during the journey. Beginning after the perturbation on June 3, I find the following differences between the two chronometers, each being the mean result from at least three comparisons, and derive from them the relative rates subjoined.

	Hohwü — Hewitt	
June 5	$+49.^s00$	
		$-0.^s37$
10	47.17	
		-0.53
15	44.50	
		-1.07
20	39.17	
		-0.92
24	35.50	

As the mean rate of Hohwü was about $+0.^s9$, these values agree fairly well with the assumed variable rate for Hewitt, which I therefore adopt as the most probable. For the middle of the period, June 12, the chronometer correction derived by means of the latter rates differs from that which would follow from the constant rate $+0.^s29$ by $1.^s36$.

A great difficulty is caused by the perturbation on June 3, when the difference between the chronometers seems to have varied abruptly

3 secs. It was probable that this must be attributed to the chronometer Hohwü, which supposition seems confirmed by the time determination at N'Kutu of June 5 if we reduce it to Chiloango with the difference of longitude determined in Dec. 1903, but it is undoubtable that we have here a source of uncertainty for the following determinations of longitude. I already remark here that I have finally accepted no jump in Hewitt and one of 2 seconds in Hohwü. For the daily rate of the latter we then must accept $+ 0^{s}.91$ instead of $+ 0^{s}.83$. In addition I remark that also for the determinations in 1904 I have assigned equal weights to the two chronometers.

3. *Determinations of longitude in* 1904.

Mayili. On June 2 I here secured a time determination by means of Sirius west, and of α Bootis east of the meridian. The results obtained from the two, corrected for division errors and flexure, differ inter se by $0^{s}.37$.

Here follow the mean results, to which I have added the corrections to the mean time of Chiloango derived by means of the adopted rates ($+ 0^{s}.91$ for Hohwü and a variable rate for Hewitt) and the difference of longitude derived thence.

June 2 $6^{h}5$ M.T. Chiloango

	Hohwü	Hewitt
Correction to M.T. Mayili	$+ 49^{m}50^{s}.89$	$+ 50^{m}36^{s}.39$
„ „ „ Chiloango	$+ 48\ 29\ .33$	$+ 49\ 17\ .08$
Difference of longitude	$-\ 1\ 21\ .56$	$-\ 1\ 19\ .31$
	Mean	$-\ 1^{m}20^{s}.44$

In 1902 I had found $- 1^{m}21^{s}.3$.

If we had derived the correction of Hohwü with a rate of $+0^{s}.83$, the difference of longitude according to this chronometer would have been $- 1^{m}21^{s}.80$, while Hewitt with an assumed constant rate would have yielded $- 1^{m}19^{s},89$.

N'Kutu. Here I was obliged to have recourse to the sun for determination of time and on June 5 I obtained the following results from 4 observations of the two limbs in the two positions of the instrument. I now begin by deriving the correction of Hohwü to the M. T. of Chiloango, without accepting a jump, and therefore with the rate $+ 0^{s}.83$.

June 5 $3^{h}.1$ M.T.

	Hohwü	Hewitt
Correction to M.T. N'Kutu	$+50^{m}28^{s}.54$	$+51^{m}17^{s}.54$
„ „ „ Chiloango	$+48\ 31\ .45$	$+49\ 18\ .30$
Difference of longitude	$-\ 1\ 57\ .09$	$-\ 1\ 59\ .24$

while the result of Dec. 1903 was $-1^{m}59^{s}.32$. From this it would appear that on June 3 a perturbation occurred in Hohwü and not in Hewitt and that the jump in the former amounts to about 2 secs., which agrees sufficiently with the observed abrupt variation in the difference between the two.

For a more accurate investigation of the perturbation I have tried to avail myself of the time determination of June 2 at Mayili, after having reduced it to Chiloango by means of the difference of longitude determined in 1902, but this has not thrown more light on the subject. Everything considered I have finally accepted as the effect of the perturbation: a jump of 2 seconds in Hohwü.

As to the longitude of N'Kutu itself, it will be best to use for it only the determination of Dec. 1903, although the new determination by Hewitt perfectly agrees with it.

Buku-Zan. My observations were made in the factory of the firm Hatton and Cookson. For a time determination I could obtain only 3 pointings at the sun's limbs on June 14. To their results I have added the corrections to M. T. Chiloango according to the adopted computation (i. e. with a jump in Hohwü and a variable rate of Hewitt) and also the difference of longitude derived from them.

June 14 $4^{h}0$ M.T.

	Hohwü	Hewitt
Correction to M.T. Buku-Zan	$+\ 50^{m}13^{s}43$	$+\ 50^{m}57^{s}93$
„ „ „ Chiloango	$+\ 48\ \ 38.12$	$+\ 49\ \ 21.22$
Difference of longitude	$-\ \ 1\ \ 35.31$	$-\ \ 1\ \ 36.71$

Mean $-\ 1^{m}36^{s}01$

Computed with constant rates and without an assumed jump the results would have been $-\ 1^{m}34^{s}51$ and $-1^{m}38^{s}02$, hence in less good harmony.

Chimbete. Also here (factory of Hatton and Cookson) I could observe only the sun for a time determination, but I secured at least a complete set of 4 observations of both limbs in both positions; the two pairs computed separately differ by $0.^{s}83$.

The results were the following; to these I have added the corrections to M. T. Chiloango according to the adopted computations, and the difference of longitude derived by means of them.

June 21 3^h6 M. T.

	HOHWÜ	HEWITT
Correction to M. T. Chimbete	$+50^m37^s73$	$+51^m15^s73$
„ „ „ Chiloango	$+48$ 44.46	$+49$ 22.52
Difference of longitude	$-$ 1 53.27	$-$ 1 53.21
Mean	-1^m53^s24	

whereas if computed with constant rates without an assumed jump. I would have got -1^m53^s03 and $-$ 1^m53^s81.

Thus the results following from the two computations differ much less than for the other places.

4. *Determinations of latitude in* 1904.

Buku-Zan. For a determination of the latitude I could observe only on June 15 one star in the south, β Centauri. Of this star I obtained 8 pointings distributed equally over the two positions.

The results were:

1st pair	$\varphi = -4^\circ\ 46'\ 4''46$
2nd „	5.51
3rd „	8.54
4th „	6.51
Mean	6.26

and after correction for division error and flexure

$$\varphi = -\mathbf{4^\circ 46' 11''.1}.$$

Chimbete. I only succeeded on June 20 in securing 10 pointings on α Crucis, distributed equally over the two positions, with the following results.

1st pair	$\varphi = -\ 5^\circ\ 1'\ 18''.40$
2nd „	18 .65
3rd „	21 .83
4th „	20 .53
5th „	19 .52
Mean	19 .78

and after correction for division error and flexure

$$\varphi = -\mathbf{5^\circ 1' 24''.5}$$

5. *Final results.*

I finally accept the following values as the most probable results of my determinations of the longitude and the latitude of the four stations in the interior. For the longitude of Mayili I take the mean of the two determinations and for that of N'Kutu I use only that of 1903.

	Latitude	Difference of longitude with Chiloango
Mayili	$-5^\circ\ 4'\ 40''$	$-1^m\ 20^s.9$
N'Kutu	-4 57 5	-1 59 .3
Buku Zan	-4 46 11	-1 36 .0
Chimbete	-5 1 25	-1 53 .2

Astronomy. — "*Contributions to the determination of geographical positions on the West-coast of Africa. III. Appendix.*" By C. SANDERS. (Communicated by E. F. VAN DE SANDE BAKHUYZEN).

6. *Modified computation of the determinations of longitude in* 1904.

For the computation of the corrections of my chronometers to the M. T. of Chiloango during my journey of June 1904 I have supposed that the chronometer of HEWITT had not been influenced by the perturbation on June 3 and that the one of HOHWÜ had advanced 2 secs.

I had adopted the value of 2 secs. chiefly in order not to exaggerate. But the result of the time determination on June 5 at N'Kutu, taking into account the modification of the rate involved in the supposition of a jump of a given amount, as well as the comparisons on June 3 render it more probable that HOHWÜ advanced 3 secs.

I shall therefore give here the results which we obtain on the latter supposition, assuming a daily rate for HOHWÜ of $+0^s.95$. I shall also show to what results we should arrive if we adopted the extreme supposition in the opposite sense, namely that HOHWÜ was not perturbed and that HEWITT had omitted 6 beats = 3 secs, and if we again assumed daily rates of both in accordance with the last supposition. This supposition is not very probable but neither quite impossible, and in this way we may at least form some idea of the still remaining uncertainty. For the rest I still hold the supposition that the rate of HEWITT has varied during the journey owing to the fall of temperature. Here follow the values obtained for the difference of longitude between the 4 stations and Chiloango:

a on the previous supposition;
b adopting for HOHWÜ a jump of 3 secs.;
c adopting a jump of 3 secs. in the opposite sense for HEWITT.

		HOHWÜ	HEWITT	MEAN
Mayili	*a*	$-1^m 21^s 56$	$19^s 31$	$-1^m 20^s 44$
	b	21.45	19.31	20.38
	c	21.80	19.66	20.73
N'Kutu	*a*	$-1^m 58^s 62$	$59^s 24$	$-1^m 58^s 93$
	b	59.39	59.24	59.32
	c	57.09	56.94	57.02
Buku Zan	*a*	$-1^m 35^s 31$	$36^s 71$	$-1^m 36^s 01$
	b	35.73	36.71	36.22
	c	34.51	35.49	35.00

		Hohwü	Hewitt	Mean
Chimbete	a	$-1^{m}\,53^{s}27$	$53^{s}21$	$-1^{m}\,53^{s}24$
	b	53.41	53.21	53.31
	c	53.03	52.83	52.93

We find in the first place that the longitude of N'Kutu on supposition b agrees exactly with the result of December 1903 which was $59^{s}.32$, and on supposition c differs strongly from it, whence appears clearly that the latter is less probable. It further appears that, with regard to the three other stations, the results on the two extreme suppositions b and c differ $1^{s}.2$ for Buku Zan and only $0^{s}.4$ for Mayili and Chimbete, while the results on suppositions a and b differ for Buku Zan $0^{s}.2$ and for Mayili and Chimbete less than $0^{s}.1$. The results from the two chronometers separately accord fairly well inter se, Mayili excepted.

As we reject the result of 1904 for N'Kutu and replace it by that of 1903 and as for Mayili we can take the mean of the results of 1902 and 1904, we find that the uncertainty caused in the final results by the perturbation is less than was to be feared.

Lastly I give here the final results obtained in this way, assuming thereby the most probable supposition b:

Difference of longitude with Chiloango

Mayili	$-1^{m}20^{s}.8$
N'Kutu	$-1\ 59\ .3$
Buku Zan	$-1\ 36\ .2$
Chimbete	$-1\ 53\ .3$

The differences with the values adopted before are at the utmost $0^{s}.2$.

Astronomy. — "*Observation of the transit of Mercury on November 14, 1907 at Chiloango in Portuguese West-Africa*". By C. Sanders. (Communicated by Dr. E. F. van de Sande Bakhuyzen).

(Communicated in the meeting of May 30, 1908).

For a short time I have possessed a telescope of Zeiss of 80 mm. aperture and 120 cm. focal length. With this telescope I intend to observe in the first place occultations of stars in order to determine the longitude of my observing station with greater precision than hitherto has been possible. For the present the telescope has an azimuthal mounting, which however soon will be replaced by an equatorial mounting with slow motions and small divided circles. In the mean time

I have been able to use the telescope for observing, at least partly, the transit of Mercury on November 14 1907, and I venture to publish my results here.

To give my telescope a firm basis I had a pier built of beton surrounded by an isolated floor and provided with a movable roof open at the sides, which roof can be entirely moved aside. For the transit of Mercury, however, I kept the roof over the instrument in order to protect myself from the burning sunbeams and especially to keep out the light from outside as much as possible.

For the observations I had constructed a projection apparatus, a kind of camera having the shape of a truncated pyramid, of which one side is open and the three others are coated with black paper. The base on which the image was to be formed was at a distance of about 14 cm. from the eye piece. The camera was adjustable in distance and in inclination, to secure the proper position of the plane of the image.

With the highest power of the telescope, 133, the diameter of the projected image of Mercury was nearly 1 mm. The fine solar spots that were present could be sharply observed and those in the neighbourhood of the western limb could be seen surrounded by very distinct faculae.

Unfortunately the beginning of the transit was hidden from my view by clouds. Towards 1 o'clock mean time of Chiloango it began to clear up and, after Mercury had been visible on the sun as a well defined disc, its egress could be observed very well. I found:

third contact at $2^h35^m38^s$ M.T. Chiloango
last „ „ 2 38 7 „ „

The moment of the 4th contact, that at which the last impression on the limb seemed to disappear, was difficult to estimate within some seconds chiefly owing to the unsteadiness of the images, but I hold that but for this unsteadiness the observation of the last internal contact could have been made with great precision. The corrections of my chronometers were derived from time determinations before and after the transit.

The times computed from the Nautical Almanac for the 3rd and the 4th contact at Chiloango were $2^h35^m47^s$ and $2^h38^m24^s$. Thence follow for the differences observation — computation: -9^s and -17^s.[1])

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[1]) (Note added by E. F. v. d. SANDE BAKHUYZEN). According to the mean of the observations made at Leiden, these differences were -6^s and -21^s. Hence the results of Mr. SANDERS agree very well with these. The greater difference for the 4th contact must probably be ascribed to the circumstance that all the observers have observed this phenomenon too early.

Zoology. — *"Some results of the investigation of the Cirripeds collected during the cruise of the Dutch man-of-war "Siboga" in the Malay Archipelago."* By Dr. P. P. C. Hoek.

Having explained the position the Cirripeds occupy in the Class Crustacea the author emphasized first of all the great advantage of possessing Darwin's well-known Monograph [1] when studying the animals of this group. This book may still be considered as a model for similar monographs, not only in treating the Sub-Class from a general point of view, but also for the description of the different species.

As might be expected the study of the material collected with the "Siboga" has considerably increased our knowledge concerning the biology, the mutual relations and the anatomy of these animals: a few interesting cases have already been communicated to the Academy [2]) and a more detailed treatment is given in the Report on the group published in the Results of the Expeditions edited by Prof. Max Weber. The first part of this Report on the Cirripeds was published in September 1907, a great deal of the second part and the determination of nearly the whole material has been achieved by this time.

To have an idea of the importance of the material collected by the "Siboga" it is worth while to compare it with that obtained during the English expedition with the "Challenger". The English man-of-war the "Challenger" made a cruise round the world, which lasted about three years and a half, and brought home collections from nearly all the oceans and seas of the earth's surface; the Cirripeds collected during that cruise were also worked up by the present author, the report on the group was published in 1883. From the accompanying table it may now be seen that the material collected by the "Siboga" in the course of one year, and, comparatively speaking, in an area of limited extension, is not inferior to that of the "Challenger"; the latter, however, collected the greater part of its spoil from the bottom of the great oceans of the world where as a rule the depth was very important. The "Siboga" on the other hand, had better opportunity to investigate coasts, reefs etc. Hence it is easily understood that whereas the "Challenger" from depths to over 5000 m. obtained a richer collection of true deepsea-animals, the "Siboga" succeeded in collecting along with an

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[1] Darwin, Ch., Monograph of the Subclass Cirripedia (in 2 Volumes). Vol. I. The Lepadidae or Pedunculated Cirripedes, 1851; Vol. II. The Balanidae (or Sessile Cirripedes); The Verrucidae etc. 1854. London: Printed for the Ray Society.

[2] Proceedings of the Academy of Sc. of June 25th, 1904 and January 27th, 1906.

COMPARISON OF THE CIRRIPEDS COLLECTED BY THE "SIBOGA", WITH THOSE OBTAINED BY THE "CHALLENGER".

Genera	Siboga: Malay Archipelago				Challenger: Voyage round the world			
	Number of species collected	Of these were novae species	Of these were collected at depths from 200—499 m.	Idem from 500—2800 m.	Number of species collected	Of these were novae species	Of these were collected at depths from 200—499 m.	Idem from 500—5130 m.
Lepas	2	—	—	—	6	—	—	—
Poecilasma	7	3	3	—	2	2	—	2 5)
Dichelaspis	5	4	—	1 1)	1	1	—	1 6)
Conchoderma	—	—	—	—	2	—	—	—
Megalasma	2	1	1	—	1	1	—	—
Alepas	5	5	1	2 2)	1	1	—	1 7)
Microlepas n. gen.	1	1	—	—	—	—	—	—
Ibla	2	1	—	—	—	—	—	—
Scalpellum	38	32	8	22	43	43	7	36
Pollicipes	1	—	—	—	—	—	—	—
Lithotrya	4	1	—	—	—	—	—	—
Balanus	±20 *)	±10 *)	3	1 3)	10	5	2	1 8)
Acasta	2	1	—	—	1	—	—	—
Tetraclita	3	—	—	—	2	—	—	—
Pyrgoma	3	2	1	—	—	—	—	—
Creusia	1	—	—	—	—	—	—	—
Coronula	—	—	—	—	1	—	—	—
Chthamalus	2	—	—	—	2	1	—	—
Hexelasma n. gen.	1	1	—	1 4)	—	—	—	—
Verruca	7	6	—	6	6	6	—	6
Total	106	68	17	33	78	60	9	47
			50 deepsea-spec.				56 deepsea-spec.	

*) Provisional determination.
1) *Dichelaspis Weberi* from a depth of 560 m.
2) *Alepas morula* from 538 m. and *Alepas ovalis* from 984 m.
3) *Balanus alatus* from 564 m.
4) *Hexelasma arafurae* from 560 m.
5) *Poecilasma carinatum* from 750 m. and *P. gracile* from 740 m.
6) *Dichelaspis sessilis* from 1800 m.
7) *Alepas pedunculata* from 740 m.
8) *Balanus hirsutus* from 900 m.

important deepsea-material, a greater number of shallow-water forms: a richer collection altogether, as many species of Cirripeds belong to the coastal fauna.

However, this table was not compiled especially to show the greater number of species collected by the Dutch expedition. Its main object is to point out that the deepsea-material of all the oceans and seas of the world together, as far as Cirripeds are concerned, has after all no other composition than that which was collected in a relatively small area, the Malay Archipelago. For both collections that composition comes to this, that after all only two genera *Scalpellum* and *Verruca*, in deeper water, are represented by numerous species and that the other genera which do occur in that deeper water are represented there by very few forms only. It is true that the genera *Scalpellum* and *Verruca*, in shallow water, are also represented by several species: we now know 125 species of *Scalpellum*, which are so-called "good" species and which in any case, almost without exception, can easily be distinguished from one another; of these 90 live at depths of over 500 m. to ca. 5000 m. and 35 in shallower water. The number of known species of *Verruca* now amounts to 36; of these 5 were observed in shallow water and 31 at depths from 500 to ca. 3400 m. In deep water, however, only these two genera found circumstances specially favourable for the formation of new species, whereas the same for other genera holds good in more shallow water. As an instance of the latter the genus *Balanus* may be pointed out: of this genus by this time over 60 species are known and, therefore, it can safely be considered as one rich in species. However, only 5 of these have been observed in water of a depth of 200—500 m. and of the latter only 2 at a depth down to 564 m. On the other hand 55 species of this genus are known, which inhabit the coast or relatively shallow water only.

The author thinks that at the present moment our knowledge is by far too incomplete to permit of an explanation of phenomena of this kind; in such cases all we can do is to try to state and to control the facts as accurately as possible and we must then confine ourselves to considering it as a peculiarity of a few genera that their numerous species divide themselves over so strongly divergent depths, whereas it is characteristic of other genera that none, or a single, or a few species only have been able to adapt themselves to somewhat more considerable depths.

It is remarkable at the same time, and this holds good for the genus *Scalpellum* especially, but for most of the known species of *Verruca* also, that such richness in species is accompanied by so great an isolation of the different forms. Of course, we cannot express our opinion on this matter with absolute certainty, as dredging, especially in deeper water, always remains an insecure method of testing the greater or lesser commonness of a species at the place where it occurs. Yet it is very striking, that in the collections made the species of Cirripeds from deeper water nearly without an exception are represented by one or by a very few specimens only. Especially when taking into consideration that the pelagic Cirripeds and those living near the coast or in shallow water, are nearly all of them characterised by numerous specimens living in the neighbourhood of one another, we are brought to admit, that where the depth is more considerable, relatively large distances separate the places, where the animals of a certain species occur, from one another, or, that specimens of such a species are never numerous and not to be found at all at very many places. This is also proved by the circumstance, that the "Siboga" found again specimens of two species of *Scalpellum* only out of the ten which were collected by the "Challenger" in the Malay Archipelago. That the "Siboga" found again the only species of *Verruco* which the "Challenger" brought home from deeper water in that area, would not be in accordance herewith — in both cases, however, that species was also represented by very few specimens only. Finally, it seems astonishing in this connection that in several cases representatives of two and three species of the genus *Scolpellum*, sometimes moreover accompanied by a single specimen of a species of *Verruca*, were obtained with the same haul of the dredge, from the very same locality in consequence. Such stations seem to be very favourable for the occurrence of these animals: however, for these found there the same holds good, viz., that they were collected in very few specimens only [1]).

For some deepsea-species of *Scalpellum* it was possible to make out, that they produced only a few but relatively large eggs, and that their metamorphosis was an abbreviated one. There is good reason to suppose that these peculiarities are of importance for the question of their scarcity — we cannot say, however, that the one is explained by the other. Nevertheless, so far as our knowledge now goes, we must consider the deepsea-species of *Scalpellum* and *Verruca* as hermits; as the number of species of these genera especially is very large, most probably they furnish precious evidence for the ideas, about the influence of isolation on the origin of new species, which were brought forward originally by MORITZ WAGNER[1]) and were criticised and adopted in a much modified form only by **WEISMANN**[2]).

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[1]) It is obvious to admit, that the condition of the bottom in such cases is all-important. Without denying it. we must point out, however, that to judge from the information regarding the condition of the bottom as given in the list of the stations, its importance for the distribution of the *Cirripedia* is by no means so apparent as might be expected. So we can well say that many species of *Scalpellum* were found at places where the bottom was muddy, but several other species were obtained from a bottom of hard sand, of coarse sand or of coral sand etc. etc.

For the geographical distribution of the Cirripeds the study of those collected by the "Siboga" has also been very instructive. With the exception of the pelagic forms, which are found attached to floating objects: pieces of wood, vessels, animals swimming at the surface: Cetaceans and others, etc. etc. and many of which are found in various parts of the world, these Crustaceans live attached to stones, shells of molluscs, corals etc.; the latter have good opportunity for active locomotion only in larval condition. But even in that condition, in consequence of their nearly microscopic size, their activity is only very limited; Nauplius- and Zoëa-larvae have limbs which enable them to move about, but more important is no doubt the distribution they are subjected to in a passive way, i. e. by means of the currents. However, even the latter distribution as a rule seems to be a very limited one: we only know very few non-pelagic Cirripeds which have a world-wide range or which occur in several of the eight provinces which were proposed by the present author in his Report on the "Challenger" Cirripeds for the animals of this group. The East-Indian or Malay Archipelago combined with the Philippines, Malacca, New-Guinea and the East coast of (British) India is one of these provinces; the investigation of the "Siboga"-material has shown again that this province indeed possesses its own Cirripeds, with the exception only of those species, which so to say spread themselves over its boundaries into other provinces, perhaps also of a few species which are at home in an adjacent province and came over its frontiers into the Malay Archipelago. Of the deepsea-Cirripeds we only know one single species, which can be said to occur at widely distant places of the earth's surface: *Scalpellum acutum*. The "Challenger" collected this species in the Atlantic Ocean (near the Azores) and in the Pacific (near the Kermadec-Islands) at a depth of 940-1800 m.; the "Talisman" also in the

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[1]) WAGNER, MORITZ, Die Darwin'sche Theorie und das Migrationsgesetz der Organismen. Leipzig, 1868.

[2]) WEISMANN, AUGUST, Ueber den Einfluss der Isolirung auf die Artbildung. Leipzig, 1872.

Atlantic (not very far from the coast of Portugal) at a depth of 1925 m.; the "Siboga", finally, at three different places in the Malay Archipelago and at depths varying from 825 to 1265 m. But this does not change the rule, which still can be accepted as general, viz. that whereas several *genera* of *Cirripedia*, and those of the deepsea in the first place, are spread over the whole surface of the earth, the *species* of Cirripeds and especially the deepsea-species have been found to possess a very local distribution only.

To close this article a few words on the relation of the deepsea-forms to the extinct Cirripeds of which fossil remains have been preserved. The material collected with the "Siboga" in this regard also fully confirmed the conclusions arrived at by the working up of the material from the "Challenger". The species of the genus *Scalpellum*, which in the deepsea are so largely represented, have their representatives already in relatively old layers of the earth-crust, in secondary as well as in tertiary formations. We can even say, that a great majority of the species of the deepsea, with regard to an important anatomical characteristic (shape and structure of the so-called carina), show the greatest affinity to the oldest fossil forms (all those found in secondary formations); for this genus, therefore, we can safely admit that the deepsea-species, at least to a certain extent, show an archaic character. Side by side with the fossil *Scalpellum*'s, in the same formations and even in the same rocks or stones, numerous species of the genus *Pollicipes* were found. To this genus of which Darwin alone enumerated 22 different fossil species belong the oldest known fossil Cirripeds and under the living it is still represented by half a dozen species. The "Challenger", however, did not succeed in collecting one single species of this genus even from slightly deeper water, which, when the author worked up the material of the "Challenger", gave rise to the remark, that the possibility of future investigations of the deepsea bringing to light species of the genus *Pollicipes*, could not be denied. Well then, the "Siboga" investigating the deepsea very carefully in one of the areas, where one of the living species of *Pollicipes* (*P. mitella*) is very generally distributed, did not obtain from deeper water one single specimen of a species of this genus either. So the exactness of the opinion pronounced in 1883, that, as far as the genus *Pollicipes* is concerned, the littoral or shallow water forms have preserved a more archaic character, has been completely confirmed by the results obtained with the "Siboga"-expedition. Of the genus *Verruca* a few species have also been found in older formations: one of these (*V. strömia*) is still living and a well-known shallow water form and was also observed in glacial deposits and in Red and Coralline Crag in England as well; a second species is found according to DARWIN in tertiary formations in Patagonia; a third (*Verruca prisca*) in the chalk of England and Belgium. As far as we know the last-named species, a certain affinity of this extinct species with several of the deepsea-species of *Verruca* cannot be denied. But for *V. strömia,* the genus *Verruca,* therefore, in this regard also would show a greater analogy with *Scalpellum* than with *Pollicipes.*

Physics. — "*Calculation of the pressure of a mixture of two gases by means of* GIBBS'*s statistical mechanics.*" By Dr. L. S. ORNSTEIN. (Communicated by Prof. H. A. LORENTZ).

By the method of statistical mechanics I have calculated in my dissertation[1] the pressure of a mixture of two gases, neglecting terms of an order higher than the first with respect to σ_1^3, σ_2^3 and σ^3. The quantities σ_1 and σ_2 are the diameters of the molecules of the gases composing the mixture, and σ has been put for $\frac{\sigma_1+\sigma_2}{2}$.

In a recent paper[2] H. HAPPEL has determined the pressure of a mixture by means of a method due to L. BOLTZMANN, retaining terms of higher order with respect to the above quantities.

As the method of statistical mechanics seems to me more exact than the one used by HAPPEL, I have been led to apply it to the problem which he has treated.

J. W. GIBBS has shown[3] that the pressure of a gas is given by the equation

$$p = -\frac{d\Psi}{dV} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where V is the volume, and Ψ what may be called the statistical free energy. We have therefore to determine this quantity Ψ.

Let us suppose that the volume V contains n_1 molecules of the first kind with the diameter σ_1 and the mass m_1, and n_2 molecules of the second kind with the diameter σ_2 and the mass m_2.

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[1] Toepassing der statistische mechanica van GIBBS op molekulair-theoretische vraagstukken. Leiden 1908.

[2] H. HAPPEL. Zur Kinetik und Thermodynamik der Gemische. Ann. der Phys. 1908 Bd. 26 p. 95.

[3] J. W. GIBBS. Elementary principles in statistical Mechanics. New-York 1902.

We suppose that the molecules are perfectly rigid and elastic and that they attract each other with forces acting at distances so great that we may consider the sphere of action as uniformly filled with matter.

For this case the value of Ψ is given by the equation

$$e^{-\frac{\Psi}{\theta}} = (2\pi\theta m_1)^{\frac{3}{2}n_1} (2\pi\theta m_2)^{\frac{3}{2}n_2} \int e^{-\frac{\varepsilon_q}{\theta}} dx_{11} \ldots dz_{2n_2} \quad . \quad . \quad (2)$$

I shall represent the coordinates of the molecule k of the first kind by x_{1k}, y_{1k} and z_{1k}, and those of the molecule l of the second kind by x_{2l}, y_{2l} and z_{2l}.

The integration has to be extended to a $3(n_1 + n_2)$-dimensional space, the notion of which is obtained if we take the $3(n_1 + n_2)$ coordinates of the centres of the molecules as cartesian coordinates of a single point, and give all possible positions to the molecules of the gas.

We must exclude from the space all those points at which a condition of one of the forms

$$\left.\begin{array}{l} (x_{1k} - x_{1l})^2 + (y_{1k} - y_{1l})^2 + (z_{1k} - z_{1l})^2 < \sigma_1^2 \\ (x_{1k} - x_{2l})^2 + (y_{1k} - y_{2l})^2 + (z_{1k} - z_{2l})^2 < \sigma^2 \\ (x_{2k} - x_{2l})^2 + (y_{2k} - y_{2l})^2 + (z_{2k} - z_{2l})^2 < \sigma_2^2 \end{array}\right| \quad . \quad . \quad (3)$$

is fulfilled.

I have proved [1]) in my dissertation that the large majority of the systems of a canonical ensemble may be considered as identical in all properties that are accessible to our means of observation. For all these equivalent or identical systems the value of the potential energy of the attractive forces is equal.

The sphere of action being uniformly filled, this quantity (ε_{q_0}) can be represented by

$$\varepsilon_{q_0} = -\frac{a_1 n_1^2 + 2 a n_1 n_2 + a_2 n_2^2}{2V} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

As to the potential energy of the repulsive forces, we need not speak of it when we take into account the conditions (3).

We shall obtain a good approximation, if, in the equation (2), we write ε_{q_0} instead of ε_q (which differs from ε_{q_0} only in a small part of the systems). By this, the exponential factor becomes a constant and we may put it before the sign of integration.

The quantity Ψ is thus expressed by the equation

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[1]) l. c. p. 14

$$e^{-\frac{\Psi}{\theta}} = (2\pi\theta m_1)^{\frac{3}{2}n_1} (2\pi\theta m_2)^{\frac{3}{2}n_2} e^{-\frac{\varepsilon_{q_0}}{\theta}} \int dx_{11} \ldots dz_{2n_2} \quad . \quad . \quad (5)$$

and its determination is reduced to the calculation of the integral on the right-hand side. Let the function $\chi(n_1, n_2)$ represent this integral.

In my dissertation I have determined this function to the degree of exactitude indicated above. Before proceeding to the determination of the terms of higher order I shall repeat the former calculation which now only wants further extension.

The $3(n_1 + n_2)$-dimensional space of integration can be decomposed into $n_1 + n_2$ threedimensional spaces, each corresponding to one of the molecules. We shall divide these spaces into elements which are small in comparison with the volume of a molecule.

In order to determine the integral defining the function $\chi(n_1, n_2)$ we decompose it into a sum of products of $n_1 + n_2$ elements chosen in the spaces in question, each space being represented in the product by one and only one element.

In order clearly to see the way in which the products are formed with the restrictions imposed by (3), we proceed as follows: We number the spaces corresponding to the molecules of the first kind from 1 to n_1, those corresponding to the molecules of the second kind from $n_1 + 1$ to $n_1 + n_2$, and we choose the elements in the order indicated by these numbers.

We have to consider that, if we have chosen for the centre of the k^{th} molecule ($k < n_1$) an element lying at a point x_{1k}, y_{1k}, z_{1k}, we must exclude from the $k + 1^{\text{th}}$ up to the n_1^{th} space those elements which are situated in spheres described with the radius σ_1 around the points of these spaces whose coordinates are equal to x_{1k}, y_{1k} and z_{1k}. Similarly we must exclude those elements from the spaces from $n_1 + 1$ up to $n_1 + n_2$, which lie within the spheres of radius σ described around the points of the spaces having for coordinates x_{1k}, y_{1k} and z_{1k}. If, further, in the space $n_1 + \nu_2$ an element has been chosen at a point with the coordinates $x_{2n_1+\nu_2}$, $y_{2n_1+\nu_2}$, $z_{2n_1+\nu_2}$ we must exclude in all following spaces the elements of spheres with radius σ_2 described around the points of those spaces having their coordinates equal to $x_{2n_1+\nu_2}$, $y_{2n_1+\nu_2}$, $z_{2n_1+\nu_2}$.

The elements in the spaces 1 to $n_1 + n_2 - 1$ having been chosen, there remains in the last space $n_1 + n_2$ a region $g_{n_1+n_2}$ for the choice of the $(n_1 + n_2)^{\text{th}}$ element.

In determining the sum we can first take together all those cases in which the elements of the spaces 1 to $n_1 + n_2 - 1$ are the same.

Considering that n_1 and n_2 are very great numbers, and that the elements have been chosen quite arbitrarily, we easily see that the quantity $g_{n_1+n_2}$ must be the same for the greater majority of the possible ways of choosing the elements in the spaces up to the $(n_1 + n_2 - 1)^{\text{th}}$, and that we may therefore write

$$\chi(n_1, n_2) = g_{n_1+n_2}\, \chi(n_1, n_2 - 1) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$g_{n_1+n_2}$ being now a quite definite quantity, which it remains to determine.

It is very easy to find a first approximation to its value. For this purpose we have only to neglect the fact that the above mentioned spheres in the $(n_1 + n_2)^{\text{th}}$ space intersect. Doing so, we find

$$g_{n_1+n_2} = V - n_1 \frac{4}{3} \pi \sigma^3 - (n_2 - 1) \frac{4}{3} \pi \sigma_2^3 \quad . \quad . \quad . \quad (7)$$

From (6) and (7) we deduce by successive reductions

$$\chi(n_1, n_2) = \chi(n_1) \prod_{1}^{n_2} \left(V - n_1 \frac{4}{3} \pi \sigma^3 - (\nu_2 - 1) \frac{4}{3} \pi \sigma_2^3 \right), \quad . \quad (8)$$

where we have affixed to the sign of the product the highest value that we have to give to the number denoted by the corresponding Greek letter. A similar notation will be used in later formulae.

It is easily seen that, with the degree of exactitude to which we have now confined ourselves, the value of $\chi\ (n_1)$ is given by

$$\chi(n_1) = \prod_{1}^{n_1} \left(V - \nu_1 \frac{4}{3} \pi \sigma_1^3 \right) \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In order to push our approximation further, we have to determine $g_{n_1+n_2}$ more accurately. We must take into account that the spheres mentioned above intersect, and that we have therefore subtracted too much from the total volume.

Now three cases are to be distinguished.

1. Intersection between the spheres of radius σ described around the points corresponding to the centres of the molecules of the first kind. The distance x of the centres cannot be less than σ_1 and must be less than $2\ \sigma$.

2. Intersection between the spheres of radius σ_2 described around the points corresponding to the molecules of the second kind. The distance of the centres must lie between σ_2 and $2\ \sigma_2$.

3. Intersection between the spheres of radius σ and σ_2 described around the points corresponding to the centres of molecules of the first and second kinds respectively. The distance x of the centres must lie between σ and $\sigma_2 + \sigma$.

I shall determine the parts corresponding to these three kinds of intersections, which have been subtracted too much from V. These parts are equal for by far the majority of the possible combinations of elements in the spaces from the first up to the $(n_1 + n_2 - 1)^{\text{th}}$. We may suppose that the distribution of the points corresponding to the centres of molecules from 1 tot $n_1 + n_2 - 1$ is uniform in the $(n_1 + n_2)^{\text{th}}$ space.

1. The number of pairs of points (corresponding to molecules of the first kind) with mutual distance lying between x and $x + dx$ amounts to

$$2\pi\, n_1^2 \frac{x^2\, dx}{V} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The common part of two spheres of radius σ having a central distance x is given by

$$\pi\left(\frac{4}{3}\sigma^3 - \sigma^2 x + \frac{x^3}{12}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Hence, the total part subtracted too much on account of these intersections is equal to

$$\frac{2\pi^2 n_1^2}{V}\int\limits_{\sigma_1}^{2\sigma}\left(\frac{4}{3}\sigma^3 x^2 - \sigma^2 x^3 + \frac{x^5}{12}\right)dx = \frac{\pi^2 n_1^2}{V}\left(\frac{8}{9}\sigma^6 - \frac{8}{9}\sigma^3\sigma_1^3 + \frac{1}{2}\sigma^2\sigma_1^4 - \frac{\sigma_1^6}{36}\right) \quad (12)$$

2. The number of pairs of points (corresponding to the centres of molecules of the second kind) with a mutual distance between x and $x + dx$ is

$$2\pi\,(n_2 - 1)(n_2 - 2)\frac{x^2 dx}{V} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The common part of the spheres is found for this case, if in (11) we replace σ by σ_2, so that we find for the part subtracted too much from V

$$2\pi^2\frac{(n_2-1)(n_2-2)}{V}\int\limits_{\sigma_2}^{2\sigma_2}\left(\frac{4}{3}\sigma_2^3 x^2 - \sigma_2^2 x^3 + \frac{x^5}{12}\right)dx = \frac{17}{16}\frac{(n_2-1)(n_2-2)}{V}\left(\frac{2}{3}\pi\sigma_2^3\right)^2 (14)$$

3. The number of pairs of points such that one point corresponds to the centre of a molecule of the first kind and one to that of a molecule of the second kind, the mutual distance lying between x and $x + dx$, amounts to

$$4\pi\, n_1\,(n_2 - 1)\frac{x^2 dx}{V} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

The common part of the spheres is now given by

$$\pi\left[\frac{2}{3}\sigma_2^3+\frac{2}{3}\sigma^3-\frac{\sigma_2^2(x^2+\sigma_2^2-\sigma^2)}{2x}-\frac{\sigma^2(x^2+\sigma^2-\sigma_2^2)}{2x}+\right.$$
$$\left.+\frac{(x^2+\sigma_2^2-\sigma^2)^3}{24x^3}+\frac{(x^2+\sigma^2-\sigma_2^2)^3}{24x^3}\right]. \quad . \quad . \quad . \quad (16)$$

and the total part subtracted too much from V by

$$4\pi^2\frac{n_1(n_2-1)}{V}\int^{\sigma+\sigma_2}\left[\frac{2}{3}(\sigma^3+\sigma_2^3)x^2-\frac{1}{2}(\sigma^2+\sigma_2^2)x^3-\right.$$
$$\left.-\frac{1}{4}(\sigma^2-\sigma_2^2)^2x+\frac{1}{12}x^5\right]dx=\pi^2\frac{n_1(n_2-1)}{V}\left(-\frac{1}{18}\sigma_2^6+\sigma_2^4\sigma^2\right). \quad (17)$$

The value of $g_{n_1+n_2}$ is found by adding (12), (14) and (17) to (7) and substituting the obtained value in (8). By successive reductions we get

$$\chi(n_1,n_2)=\chi(n_1)\prod_1^{n_2}\left[V-n_1\frac{4}{3}\pi\sigma^3-(\nu_2-1)\frac{4}{3}\pi\sigma_2^3+\right.$$
$$\frac{n_1^2}{V}\pi^2\left(\frac{8}{9}\sigma^6-\frac{8}{9}\sigma^3\sigma_1^3+\frac{1}{2}\sigma^2\sigma_1^4-\frac{1}{36}\sigma_1^6\right)+$$
$$\left.+\frac{17}{36}\frac{(\nu_2-1)(\nu_2-2)}{V}\pi^2\sigma_2^6+\frac{n_1(\nu_2-1)}{V}\pi^2\left(-\frac{1}{18}\sigma_2^6+\sigma_2^4\sigma^2\right)\right] \quad (18)$$

It is easily seen that to the degree of approximation now required, $\chi(n_1)$ is represented by

$$\chi(n_1)=\prod_1^{n_1}\left(V-(\nu_1-1)\frac{4}{3}\pi\sigma_1^3+\frac{17}{36}\frac{(\nu_1-1)(\nu_1-2)}{V}\pi^2\sigma_1^6\right). \quad (19)$$

Substituting these values in (5), taking the logarithm of the result, and developing this logarithm in ascending powers of $\frac{1}{V}$, we find

$$-\frac{\Psi}{\theta}=C+\frac{a_1n_1^2+2an_1n_2+a_2n_2^2}{2\theta V}+$$
$$+\sum_1^{n_1}\left[\log V-\frac{\nu_1-1}{V}\frac{4}{3}\pi\upsilon_1^3-\frac{(\nu_1-1)(\nu_1-2)}{V^2}\frac{15}{36}\pi^2\sigma_1^6\right]+$$
$$+\sum_1^{n_2}\left[\log V-\frac{n_1}{V}\frac{4}{3}\pi\sigma^3-\frac{(\nu_2-1)}{V}\frac{4}{3}\pi\sigma_2^3-\frac{(\nu_2-1)(\nu_2-2)}{V^2}\frac{15}{36}\pi^2\sigma_2^6-\right.$$
$$-\frac{8}{9}\frac{n_1^2}{V^2}\pi^2\sigma_1^3\sigma^3+\frac{1}{2}\frac{n_1^2}{V^2}\pi\sigma^2\sigma_1^4-\frac{1}{36}\frac{n_1^2}{V^2}\pi^2\sigma_1^6-$$
$$\left.-\frac{16}{9}\frac{n_1(\nu_2-1)}{V^2}\pi^2\sigma_2^3\sigma^3+\frac{n_1(\nu_2-1)}{V^2}\pi^2\sigma_2^4\sigma^2-\frac{1}{18}\frac{n_1(\nu_2-1)}{V^2}\pi^2\sigma_2^6\right] \quad (20)$$

C being the part which is independent of V.

Since n_1 and n_2 are very large numbers, we easily see that the expression (20) can be transformed to

$$
\begin{aligned}
-\frac{\Psi}{\theta} = C + \frac{\alpha_1 n_1^2 + 2\alpha n_1 n_2 + \alpha_2 n_2^2}{2\theta V} + (n_1+n_2)\log V - n_1^2\frac{\beta_1}{V} - \frac{5}{16}n_1^3\frac{\beta_1^2}{V^2} \\
- n_2^2\frac{\beta_2}{V} - \frac{5}{16}n_2^3\frac{\beta_2^2}{V^2} \\
- 2n_1 n_2\frac{\beta}{V} \\
-\frac{8}{9}\frac{n_1^2 n_2}{V^2}\pi^2\sigma_1^3\sigma^3 + \frac{1}{2}\frac{n_1^2 n_2}{V^2}\pi^2\sigma_1^4\sigma^2 - \frac{1}{36}\frac{n_1^2 n_2}{V^2}\pi^2\sigma_1^6 \\
-\frac{8}{9}\frac{n_1 n_2^2}{V^2}\pi^2\sigma_2^3\sigma^3 + \frac{1}{2}\frac{n_1 n_2^2}{V^2}\pi^2\sigma_2^4\sigma^2 - \frac{1}{36}\frac{n_1 n_2^2}{V^2}\pi^2\sigma_2^6 \quad . \; . \; (21)
\end{aligned}
$$

where β_1 has been put for $\frac{2}{3}\pi\sigma_1^3$, β_2 for $\frac{2}{3}\pi\sigma_2^3$ and β for $\frac{2}{3}\pi\sigma^3$.

Finally, differentiating Ψ with respect to V, we find the following equation for the pressure

$$
\begin{aligned}
\frac{p}{\theta} = \frac{n_1+n_2}{V} + \frac{n_1^2\beta_1}{V^2} + \frac{5}{8}\frac{n_1^3\beta_1^2}{V^3} + \frac{n_2^2\beta_2}{V^2} + \frac{5}{8}\frac{n_2^3\beta_2^2}{V^3} + \frac{2\,n_1 n_2\beta}{V^2} \\
-\frac{n_1^2 n_2}{V^3}\beta_1^2\left(-4\frac{\beta}{\beta_1} + \frac{9}{4}\frac{\beta}{\beta_1}\frac{\sigma}{\sigma_1} - \frac{1}{8}\right) \\
-\frac{n_1 n_2^2}{V^3}\beta_2^2\left(-4\frac{\beta}{\beta_2} + \frac{9}{4}\frac{\beta}{\beta_2}\frac{\sigma}{\sigma_2} - \frac{1}{8}\right) \\
-\frac{\alpha_1 n_1^2 + 2\,\alpha n_1 n_2 + \alpha_2 n_2^2}{2\,\theta V^2}.
\end{aligned}
$$

The quantity θ is proportional to the absolute temperature.

The expression for p is of course symmetrical in the quantities relating to the two kinds of molecules, and it would have been possible to find the same result by arranging the spaces in a different order. Our result agrees with that of HAPPEL, the only difference being in the notations.

Botany. — "*Lindeniopsis. A new subgenus of the Rubiaceae*". By Dr. Th. Valeton (Buitenzorg).

During an official journey through the island of Billiton in March 1907 Mr. Ham, Inspector of Forests in the Dutch East Indies, gathered a small, but not unimportant herbarium collection, which he gave over to me for study.

The importance of this collection mainly depends on the fact, that it was formed on lands, which are extremely rare in the Indian Archipelago, and are as yet florally almost unknown. These are the socalled "*padang*" lands (compare Verbeek in Jaarboek Mijnwezen 1897, p. 60 and 61). The soil of these lands consists of young, loose sediments of recent origin, namely quartz sand and clay, both often containing iron and manganese; the soil, however, owes its peculiar character to the presence of a mineral, which the Chinese call *fo sau kak* and which consists of quartz sand, which has been moulded together by organic acids into a pretty firm, dark brown sand-stone.

"These *padang* lands are characterized by a sparse and peculiar vegetation, in consequence of the small permeability to water of the "*fo sau kak*", so that level padang-lands are frequently inundated after heavy rains, and the roots of the plants, which can only penetrate with difficulty into the hard "*fo sau kak*", rot and die off." (Verbeek l.c.).

Besides in Billiton, these padang soils are also found in Banka between Doeren and Boekit (Verbeek l.c.). In other parts of the Archipelago they do not appear to be known. The most important of these lands are found in the north and north-east of the island, between Boeding and Manggar, and were studied botanically by Mr. Ham.

From verbal information and from the journal of the voyage, which Mr. Ham kindly lent me for perusal, I obtained the following data:

The appearance of the padang soils is not everywhere the same. Mr. Ham distinguishes: 1 *grass padang*, often rich in flint, where grasses and sedge-grasses predominate, 2 *fern padang* where ferns (*Pteris aquilina L.*, *Nephrolepis acuta* Presl.), form almost the whole vegetation, being only mixed with *Xyris microcephala* Hassk., *Fimbristylis* spec., *Melastoma* spec., *Calophyllum pulcherrimum* Wall., *Psychotria viridiflora* Bl. and 3 *sand padang*, where the soil consists of blinding white quartz sand. The white layer varies in thickness from $^1/_2$—5 centimetres; under this the soil is grey, obviously through humus, and sometimes it is grey immediately below the surface, when fine, black humus or mosses occur at the bottom. The vegetation nowhere forms a compact mass or sod. Groups of low and high shrubs, generally with higher shrubs or small trees in the middle, alternate with a lower vegetation, which is also always limited to separate spots or clumps, so that the white sand can everywhere be seen through it, and in many places even has the upper hand. Of the plants which were collected here, the following are mentioned as characteristic:

Drosera Burmanni Vahl. in the dampest parts, forming dark-red areas, when seen from a distance, often placed on small columns of sand; *Fimbristylis* spec., *Rhynchospora* spec., *Xyris microcephala* Hassk. and *Xyris bancana* Miq.; more rarely *Salomonia oblongifolia* D.C., *Lindernia stemodioides* Miq., *Thuarea sarmentosa* Pers.

Of the shrubs the following are prominent: *Baeckea frutescens* L., which in low-lying padangs forms more than half of the vegetation, and reminds one very much of the *Calluna* of European heaths, *Jambosa buxifolia* Miq., *Leptospermum flavescens* Sm., *Leucopogon malayanus* Jack., *Vaccinium malaccense* Wight, *Cratoxylon glaucum* Korth., *Calophyllum pulcherrimum* Wall., *Timonius* spec., *Garcinia bancana* Miq., *Syzygium variifolium* Miq., the last three arborescent.

On the lowest lying padangs south of Manggar and near Boeding, where *Baeckea frutescens* and *Fimbristylis* spec. formed the chief vegetation, *Ischaemum* spec., *Archytaea Vahlii* Choisy, *Wormia suffruticosa* Griff., *Melaleuca minor* Sm. and a non-determinable species of *Eugenia* were also noticed; in addition mosses and lichens. Further there were collected in these localities *Rhodomyrtus tomentosa* Wight, *Nepenthes* spec., *Tristania obovata* R. Br., *Dischidia* spec. *Bromheadia palustris* Lindl. [Orchidea], *Isachne australis* R. Br. *Burmannia bancana* Miq., a species of *Lucinaea*, which is probably new, and finally a new Rubiacea, about which I wish to make a communication here.

The above-described formation has in consequence of the predominant occurrence of the Calluna-like *Baeckea frutescens* a superficial resemblance to the sandy and boggy heaths of Northern Europe. Already Junghuhn, in his description of the Battak countries I, p. 158, refers to an Erica, which above the forest zone characterizes the alpine flora in company of other woody Myrtaceae, and he doubtless means *Baeckea frutescens*. From Southern China and the Philippines to New-Guinea, where Beccari found the plant at Goldfinck Bay (altitude?) and Wichmann on the G. Siëp at about 800 Meters, the area of distribution of this species extends; it is wanting in Java and its nearest allies (numerous *Baeckea*-species) inhabit Australia.

Everywhere it is characteristic of physiologically dry plateaus and rarely descends to the low-lying plains, as in the present case. *Drosera* and the *Cyperaceae* also tend to emphasize the resemblance to heaths.

Through the other vegetation, of which the sclerophyllous and sclerocarpous Myrtaceae form an important constituent, this formation, however, approximates much more to that which was called by SCHIMPER (Pflanzengeogr. p. 538) "*Hartlaubformation*" and of which he describes a number of regions, occurring round the Mediterranean, in California, in Chili, in South-Africa and in South-Australia. These regions are all characterized by dry and hot summers, alternating with moist winters. Hence climatologically there is little resemblance between these and the padang-formation of Banka and Biliton, where it rains almost the whole year. As regards the condition of the soil, there is, on the other hand, a resemblance with the South-Australian "*scrublands*", described by SCHOMBURGK in his Flora of South-Australia 1875. (See SCHIMPER l. c. p. 559).

The dominant influence of the soil on the character of the formation cannot here be doubted; this influence, which according to SCHIMPER is relatively rare in the Tropics, has been but little investigated. (See SCHIMPER l. c. p. 405. Edaphische Wirkungen in den Tropen).

The padang-formation does not correspond even roughly with any of the vegetation-pictures and formations, mentioned in that chapter. As has been mentioned, it can only, to some extent, be compared with tropical alpine floras and with the "*Hartlaubformation*".

The plants, collected by Mr. HAM, probably do not represent a complete, but nevertheless give a very typical picture of this rather poor flora. As regards the distribution of these plants, it is at once noticeable, that not a single one of these occurs in Java, with the exception of two wide-spread grasses, which have crept in from the beach, namely *Thuarea sarmentosa* and *Isachne australis*, and with the exception of the two pantropic ferns and of *Psychotria viridiflora*, which plants were, moreover, not found in the typical sand padang. A wide distribution from Malacca to Australia through the northern part of the Archipelago, but excluding Java (probably up to and including Timor), is observed in the case of *Baeckea frutescens*, and also of *Leptospermum flavescens*, *Rhodomyrtus tomentosa*, *Melaleuca minor*, *Drosera Burmanni*, *Salomonia oblongifolia* and *Bromheadia palustris*. From Malacca and Borneo are known: *Calophyllum pulcherrimum*, *Garcinia bancana*, *Vaccinium malaccense*, *Leucopogon malayanus*, *Archytaea Vahlii*, *Wormia suffruticosa*. From Banka and Billiton only the following are known: *Jambosa buxifolia*, *Syzygium variifolium*, *Tristania obovata*, *Schima bancana*, *Xyris bancana* and *Lindernia* (Vandellia) *stemodioides*; *Cratoxylum glaucum* and a *Lucinaea* spec. nova were only known from Borneo. The as yet undetermined *Eugenia*, *Nepenthes*, *Dischidia* and *Ischaemum*, and a few others, are doubtful in this respect.

Endemic, as far as our present knowledge extends, is only the new species, now to be described. Unfortunately data are wanting about the dimensions and habit of this plant, but it belongs to the suffructicose inhabitants of the low sand-padangs, referred to above; it is among the species, poor in individuals, and it reaches a height of $^{3}/_{4}$—2 metres. The rod-like erect branches which are often 60 centimetres long, and bear at their tops the crowded inflorescences with grey hairs, the small stiff, aciculate, erect leaves, all these characters indicate a strongly xerophytic nature.

At the first examination this species seemed to me to constitute a completely new genus. It belongs to the tribe *Cinchoneae* of the sub-order *Cinchonoideae* (K. SCHUMANN), and to the sub-tribe *Hillieae*. On applying the analytical key, prepared by K. SCHUMANN (Natürl. Pflanz. Fam. IV 4 p. 42) one does not arrive at any genus in particular, but in the immediate neighbourhood either of *Cosmibuena* RUIZ and PAVON, or of *Coptosapelta* KORTH., according as to whether one takes the style to be little or very much longer than the corolla-tube. A closer comparison with the genus *Cosmibuena*, to which a small number of Central- and South-American, epiphytic shrubs belong, at once, however, reveals considerable differences in the structure of the calyx, stamens, stigma and in the dehiscence of the fruit, so that there can be no question of a union with this genus, although in habit and in the shape of the flowers the agreement is closer than with *Coptosapelta*. As regards the latter genus, it is said in the above-mentioned key: "style quadrangular and hairy", so that, if one were to adhere strictly to this, one would be forced to set up a new genus for our species, in which the style is cylindrical and glabrous. On further comparison with the characters given in the generic diagnosis for *Coptosapelta*, the following differences are also found: Calyx, small, saucer-shaped, five-toothed in *Coptosapelta*; in the new species much longer than the calyx-tube, divided to its base into five lanceolate, pointed, erect divisions. — Corolla-tube very short, as long as or shorter than the lobes of the limb, and hairy at the tube-mouth, in *Coptosapelta*; in the new species 4—6 centimetres long, thin and straight, much longer than the lobes of the limb, and glabrous at its mouth. — Anthers almost as long as the lobes of the limb and hirsute on their dorsal side, with deeply cleft base, in *Coptosapelta*; here much longer than the lobes of the limb, glabrous, and with a two-lobed base. Seeds with a regularly fringed wing in *Coptosapelta*; here surrounded by an entire wing. Finally as regards the habit, the two known species of *Coptosapelta* are high-climbing shrubs with fairly large leaves and many-flowered pendulous panicles of small flowers, whereas the new species is a small erect shrub with erect cymes of few, prominent flowers.

Superficially there seems therefore abundant reason for setting up a new genus for this new species, and on account of the great resemblance in habit, leaves, inflorescence, calyx and corolla, to the American genus Lindenia, which belongs to the tribe of the *Rondeletieae*, I gave it the name *Lindeniopsis*.

A closer comparison with *Coptosapelta flavescens* KORTH, which occurs in Java, induced me, however, to withdraw this genus and to bring the new species under *Coptosapelta*. Some of the points of difference, deduced from the literature, proved to be the result of errors in the existing descriptions. For instance, the style in *C. flavescens* is not *quadrangular* and *hairy* as described by SCHUMANN, but, except at the top, cylindrical and glabrous, as in the new species; the calyx is not saucer-shaped, but deeply divided into five divisions, and resembles, except in size, that of the new species, and the mouth of the tube is not hairy, but quite glabrous. In this way a number of the enumerated points of difference already disappear.

There is further perfect similarity in the structure of the ovary and fruit of the two plants. The very peculiar stigma, which in contradistinction to the neighbouring genera, is not two-lobed, but quite entire, and receives pollen on the stigmatic papillae which cover the whole of its hairy surface. The anthers are identical in structure and in their mode of attachment. Finally, what is very important, the pollen of the new species has, like that of *C. flavescens*, an exine with net-shaped thickenings of wide mesh, and, as would appear from the figures in the Flora brasiliensis, the plant herein differs completely from the other genera of the *Hillieae*. Having regard to all these similarities, there can be no doubt, that our new species must be included in the genus *Coptosapelta*, but forms in it a special, monotypic sub-genus.

As a morphological peculiarity, which confirms the relationship to *C. flavescens*, I here draw attention to the glands, which alternate with the calyx divisions, and have, as far as I know, not yet been described in any other of the *Rubiaceae* (with the possible exception of *Dichilanthe* HOOK.).

They have the same structure as the colleters, resembling intestinal glands, which in this genus, as in most Rubiaceae, are placed at the inside of the base of the stipules[1]) and are also found on the leaf base in *Apocynaceae* and in *Loganiaceae*. They are found in the new species, as in *C. flavescens*, alternating with the calyx divisions singly or two together; in the latter species they are however, only $^{1}/_{5}$ mm. long and have hitherto been overlooked by investigators; in the new species they are well over 1 to 1.5 m.m. in length.

Perhaps, on closer examination, they will also be found to exist in other *Rubiaceae*. Obviously they must be interpreted as rudimentary stipules of the sepals.

Coptosapelta KORTH. Descriptio nova: Calycis tubus ellipsoïdeus, limbus eo nunc brevior nunc duplo longior, persistens, dentatus vel ad basin usque 5-partitus, segmentis erectis imbricatis cum glandulis parvis stipularibus erectis teretibus singulis vel binis alternantibus. Corolla coriacea tomentosa, hypocraterimorpha, tubo brevi vel longo, gracili, tereti, intus glabro vel fauce hirta, limbi lobi obovato-lineares aestivatione contorti. Stamina 5 ori corollae inserta, filamentis brevibus subulatis; antherae oblongae vel lineares apice apiculatae, basi subbilobae vel bipartitae glabrae vel dorso hirsutissimae, dorso prope basin affixae, patentes demum saepe tortae. Pollinis granula subglobosa, poris 3?, insigniter reticulata. Discus carnosus cupularis. Ovarium biloculare. Stylus teres glaber elongatus corollae tubum aequans apice exsertus. Stigma magnum integrum, fusiforme velclavatum, in alabastro per longitudinem striatum, puberulum; ovula in loculis numerosa, placentis magnis septo affixis peltatis linearibus apice et basi liberis dense imbricatim affixa, peltata, marginata, ascendentia. Capsula obovoidea lateraliter compressa obsolete costata calyce longius persistente coronata, glabrescens ad medium versus loculicide bivalvis, vel demum saepe quadrivalvis. Semina placentae cylindricae, subcarnosae, loculum implenti extus affixa, peltata, imbricata, erecta, testa membranacea in alam hyalinam nunc insigniter fimbriatam nunc subintegram crenulatam radiatim striulatam expansa, albumine carnoso; embryo rectus parvus radicula tereti infera.

Frutices nunc alte scandentes nunc parvi erecti, canescenti-sericeo-villosi, ramulis tetragonis foliis coriaceis, subtus ± villosulis. Stipulae interpetiolares parvae ovato-trigonae.

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[1]) Vide SOLEREDER, Anat. Charakt. der Rubiaceae 1893, p, 179.

Cymae terminales et in axillis superioribus trichotomae nunc densiflorae et ample paniculatae pendentes, nunc pauciflorae erectae. Flores brevissime pedicellati, bracteolis (prophyllis) 2, pedicello insertis calyce appressis eoque brevioribus instructi, nunc parvi nunc conspicui.

Subgenus I *Eucoptosapelta* VAL. Calycis limbus ovario brevior. Corollae tubus brevis, limbi lobos aequans vel illo brevior, faucis orificium glabrum vel hirsutum. Antherae lineares, basi bifidae, dorso dense villosae, demum tortae. Stigma elongato-fusiforme vel quadrangulare. Seminum ala fimbriata. Frutices alte scandentes ramulis subteretibus. Foliis majusculis patentibus subtus ad nervos villosis. Paniculae terminales foliatae multiflorae, densiflorae, pendentes.

1. *C. flavescens* KORTH., (*Stylocoryne racemosa* haud CAVANILLES, MIQ.; *St. tomentosa* BL.): Corollae tubus limbi lobos circiter aequans, faux glabra. Calycis tubus brevis.

Habitat: Malacca, Burma, Borneo, Java.

2. *C. Griffithii* HOOK.: Corollae tubus limbi lobis multo brevior. Faux dense hirsuta. Calycis tubus elongatus.

Habitat: Malacca, Singapore.

Subgenus II. *Lindeniopsis* VAL. Calycis limbus ovario plus duplo longior, ad basin usque partitus segmentis erectis lanceolatis acutis. Corollae tubus gracilis lobos pluries superans, faucis orificio glabro. Antherae oblongae basi bilobae, glabrae. Stigma magnum, clavatum. Seminum ala subintegra.

Frutices parvi erecti, ramulis acute tetragonis erectis elongatis, foliis parvis erectis rigide-coriaceis, spinuloso-apiculatis subtus appresse villosis. Cymae terminales et in axillis superioribus trichotomae, pauciflorae, erectae.

3. *C. Hammii* VAL. Characteres subgeneris.

Habitat: Biliton.

Botany. — "*Contribution N°. 1 to the knowledge of the Flora of Java.*" (Third Continuation)[1]). By Dr. S. H. KOORDERS.

§ 6. Further data concerning Oreiostachys Pullei Gamble.

§§ 1. Additions and corrections to p. 674—686 of the "Proceedings".

The proof-corrections, which Mr. GAMBLE sent me from England last April, were, nevertheless, much to my regret, received by the printers too late for incorporation in the number of the Proceedings

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[1]) Continued from p. 773 of the Proceedings of the Royal Academy of Sciences, Amsterdam, ordinary meeting of the Math. and phys. section April 9 h 1908.

of the Royal Academy of Sciences, which appeared in April 24th 1908. I now append these proof-corrections, which date from last April and are due to Mr. J. S. GAMBLE, to whom I tender my thanks:

p. 683 line 11 from bottom: *after* Kurz, *insert:* Munro in Trans. Linn. Soc. London. XXVI. 146.

p. 683 line 4 from bottom: *before* (GAMBLE msc.) *insert*: and possibly. so establishing a connection between it and the *Schizostachyum*, the description of which by HASSKARL and KURZ are somewhat imperfect".

p. 683 line 4 from bottom: *after* additional *insert*: material.

p. 684 line 16 from bottom: *before* conspecific *insert:* very probably.

§§ 2. On the fruits of Oreiostachys GAMBLE, which have been discovered by Mr. K. A. R. BOSSCHA.

On p. 684 of the English edition of the Proceedings of the Royal Academy of Sciences, Amsterdam, meeting of February 28th 1908, it was pointed out by me, that it might be possible to trace this species locally by means of the constant native name, i. a. in order to obtain the fruits, as yet unknown.

I am now privileged to announce the collection of these fruits, as yet unrecorded in the literature, and to communicate certain further details, taken from a letter of Dr. TH. VALETON, dated Buitenzorg May 12th 1908 and from the enclosures to his letter, for which I here wish to thank him.

"Enclosed I am sending you three fruits of *Oreiostachys* GAMBLE, of which ten were sent me in November 1903 by Mr. K. A. R. BOSSCHA, after I had received in May flowers from the same station. I propose that you should send these to Mr. GAMBLE, in order that he may complete his generic description, which has been published by you. I am also sending you some notes about observations, made in the locality by Mr. BOSSCHA, and further some references to the literature, which already exists about this species." (Dr. VALETON msc. May 12th 1908).

I quote below the paragraphs in the letter referring to the observations of Mr. BOSSCHA.

"Mr, BOSSCHA drew my attention to the fact, that the plant bears flowers in two ways, namely at the end of small branches[1]) with thick foliage and also close to the stem on quite leafless lateral branches."

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[1]) Mr. GAMBLE and I have not, as yet, had at our disposal these thick-leaved branches, flowering at their ends, but only the sterile leafy branches of JUNGHUHN and the almost leafless flowering twigs, without fruits, of PULLE described by Mr GAMBLE.

"Mr. Bosscha also told me, that when he arrived in Malabar in 1896, old natives, who were thoroughly familiar with the forests of the district in which the plant occurs, were ignorant of the fact, that this bamboo had ever flowered. In 1902 the flowering began, and it recurred fairly regularly until 1906. Since then the species has died off in most places, and is now decidedly scarce. This year it has again, however, been found in flower in Taloen (a plantation on the Malabar) in May 1908."

"Now, however, young plants are beginning to appear every where, obviously self-sown."

"This phenomenon partly agrees therefore with what has been observed in the case of other bamboo-species in British India, although the flowering period has been especially long in this case". (Dr. Valeton msc. May 12th 1908).

While I here refer with special appreciation to the fact that Dr. Th. Valeton placed the three fruits and the above-mentioned data at my disposal, I need scarcely say, that I at once complied with his request, and sent the fruits, received by me on June 17th to Mr. Gamble. Although the examination of the fruits is not yet complete, and will be referred to later, as soon as the supplementary diagnosis by Mr. Gamble shall have been received, I nevertheless consider the discovery, by Mr. K. A. R. Bosscha, of the fruits of this bamboo-species of sufficient importance to call for attention here. It is evident from Dr. Valeton's letter quoted above that the receipt by him at Buitenzorg from Mr. Bosscha of the fruits of *Oreiostachys* Gamble with the flowers (the fruits having remained unknown in the literature until now) was prior to Mr. Gamble's discovery of the type of a new genus in the flowers collected by Dr. Pulle.

It may further be mentioned, that the fruits discovered by Mr. Bosscha, and the flowers collected by Dr. Pulle on the. Wajang-Windoe in 1906, are from the same district, namely the locality mentioned on p. 686 of these Proceedings.

In an enclosure to his letter to me of May 12th Dr. Valeton gives certain specific names, which he regards as synonyms (Bambusa elegantissima Hassk., etc.) and also the other literature references relating to this subject. Since these names, and the literature references, with the exception of "Munro" (see above, §§ 1), have already been published by Mr. Gamble and myself in the Proceedings of April 24th, it seems to me unnecessary to repeat them.

Although I have not had at my disposal the terminally flowering branches with thick foliage collected by Mr. K. A. R. BOSSCHA, on which Dr. VALETON's addition to GAMBLE's diagnosis is based, I can now conform this amplification of GAMBLE's diagnosis, sent me on May 12th by Dr. VALETON, thanks to supplementary material received to-day (June 27th 1908) from Dr. A. PULLE (Utrecht) and at once forwarded to Mr. GAMBLE. In order to complete the diagnosis of *Oreiostachys*, and to settle the question of the further probable synonymy of this interesting species, a question raised by Mr. GAMBLE and myself in the Proceedings of April 24th there now only remain as desiderata the collection of stem-sheaths and the examination of the authentic specimens of *Bambusa elegantissima* HASSK. and *Schizostachyum elegantissimum* (HASSK.) KURZ, which so far have not been found, either by Dr. VALETON at Buitenzorg, or by myself at Leiden or Utrecht.

Leiden, June 27th 1908.

Physics. — "*On the law of molecular attraction for electrical double points*". By Prof. J. D. VAN DER WAALS Jr. (Communicated by Prof. Dr. J. D. VAN DER WAALS).

Several physicists have already urged the supposition that the molecular attraction results from the electric forces exercised by electrically charged particles which are contained in the molecule. One of the simplest suppositions we can make in trying to explain the molecular action from an electrical origin is that the molecules will behave as electrical double points. This has, in fact, been assumed by Mr. REINGANUM[1] and by Mr. SUTHERLAND[2].

As the formula for the action between two electrical double points, which is the same as that for the action between two magnetic molecules[3], contains $\frac{1}{r^4}$ as a factor, — r representing the distance between the two double points, — these physicists concluded that the molecules would attract one another with a force proportional to $\frac{1}{r^4}$. The opinion that the electron-theory supports the supposition of a molecular attraction proportional to $\frac{1}{r^4}$ has accordingly been often advanced.

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[1] M. REINGANUM, Phys. Zeitschr. 2, 241 (1901); DRUDES Ann. 10, 334 (1903).

[2] W. SUTHERLAND, Phil. mag. (6) 4, 625 (1902).

[3] Cf. J. C. MAXWELL, A treatise on electr. and magn. Art. 387.

On closer inspection, however, this opinion proves to be unfounded. If the double points have not yet yielded to the directing couples which they exercise on one another, and if therefore the axes may be directed in any direction, the mutual action will as often be a repulsion as an attraction, i. e. the mean attraction will be zero. If on the other hand we might assume that they had perfectly yielded to the directing couples, they would attract each other with forces proportional to $\frac{1}{r^4}$. It is, however, evident that the molecules will only partially have yielded to the couples, and that they will be more perfectly directed according as they have approached each other more closely and therefore lie in a stronger field of forces. The consequence will be that the resulting molecular action will be an attraction which with increasing r varies more rapidly than $\frac{1}{r^4}$. This circumstance has not escaped the attention of REINGANUM and of SUTHERLAND. They, however, thought that the law of attraction would only slightly deviate from $\frac{1}{r^4}$ and assumed this law to be, at least approximately, accurate.

In 1900 the present writer expressed the supposition that the resulting attracting forces would vary more rapidly than $\frac{1}{r^7}$ [1]). It is true that he founded his calculation on a somewhat different supposition as to the nature of the molecules, namely that they would act not as constant but as periodical double points, but this difference is probably not essential, as the law of attraction for vibrating double points will not improbably agree in a high degree with the law for constant double points, at least when the mutual distance of the molecules is small compared with the wave-length, which condition is satisfied in the case of gas-molecules at pressures of the order of one atmosphere.

At present it is my intention to investigate more accurately what will be the law of the resulting attraction for constant double points. We shall see that the attraction in this case really varies more rapidly than proportional to $\frac{1}{r^7}$. To render a rigorous treatment of this problem possible, we shall assume the following condition to be satisfied :

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[1]) J. D. VAN DER WAALS Jr., Dissertation, Amsterdam, p. 85.

1st. The molecules are electrical double points with a constant moment m.

2nd. The mean distance of the molecule is so great that we may neglect the cases in which more than two molecules interact.

3rd. The velocities and the accelerations of the molecules have a value relatively so small, that we may assume that their field of force does not differ appreciably from the electrostatic field of the double points. A consequence of this supposition is that the energy of the system may be represented by:

$$L - {}^1/_2 \Sigma\, m\, \mathfrak{E} \cos \varphi + C$$

where L represents the kinetic energy of the system, $\mathfrak{E}$ the electric force, φ the angle between the axis of a molecule and the electric force at that place, and C a constant which does not depend on the velocity and the mutual position of the molecules.

If this last condition is satisfied the statistical mechanical considerations of Boltzmann and of Gibbs are directly applicable to our problem. If on the other hand it is not satisfied these considerations cease to be applicable and then it is impossible to solve the problem before a statistical treatment of a continuum as the electromagnetic field has been worked out, which is analogous to Gibbs's treatment of systems with a finite number of degrees of freedom; this however is not the case as yet. A rigorous discussion of the case that the molecules are vibrators is therefore as yet impossible and so we shall have to confine ourselves to the supposition of constant double points.

Let us imagine a molecule A and at a distance r another molecule B. The angle between the axis of A and the radius vector will be called ϑ, then the electric force exerted by A at the point where the molecule B is found, will be:

$$\mathfrak{E} = \frac{m}{3r^3} \sqrt{4 \cos^2 \vartheta + \sin^2 \vartheta} = \frac{m}{3r^3} \sqrt{3 \cos^2 \vartheta + 1.}$$

If again φ is the angle between $\mathfrak{E}$ and the axis of B then the potential energy of B is:

$$-\frac{m^2}{3r^3} \sqrt{3 \cos^2 \vartheta + 1} \,.\, \cos \varphi$$

According to the well-known theory of Boltzmann and Gibbs the probability that the angle φ will fall between the limits φ and $\varphi + d\varphi$ and the angle ϑ between the limits ϑ and $\vartheta + d\vartheta$ is:

$$
{}^1/_4 \sin \varphi\, d\varphi \,.\, \sin \vartheta\, d\vartheta \,.\, e^{\frac{m^2 \sqrt{3 \cos^2 \vartheta + 1} \,.\, \cos \varphi}{3 r^3 t}} ,
$$

where t represents twice the mean kinetic energy for one degree of freedom or $\frac{2}{3}$ of the mean kinetic energy of the motion of the centre of gravity of a molecule. So we find for the mean value of the potential energy of a molecule at a distance r from another molecule:

$$E = -\int_0^\pi\int_0^\pi \frac{m^2}{3\,r^3}\sqrt{3\cos^2\vartheta+1}\;\cos\varphi\,.\,e^{\frac{m^2\sqrt{3\cos^2\vartheta+1}\,.\,\cos\varphi}{3\,r^3 t}}\,\frac{1}{4}\sin\varphi\,d\varphi\,.\sin\vartheta\,d\vartheta.$$

or [1])

$$E = +\frac{t}{4}\int_0^\pi \sin\vartheta\,d\vartheta\int_0^\pi \cos\varphi\,.\,de^{\frac{m^2\sqrt{3\cos^2\vartheta+1}\,.\,\cos\varphi}{3\,r^3 t}}$$

Let us put $\frac{m^2}{3\,r^3\,t} = c$ and $\sqrt{3\cos^2\vartheta+1} = x$, then we find by partial integration:

$$E = -\frac{t}{4}\int_0^\pi \sin\vartheta\,d\vartheta\left\{e^{cx}+e^{-cx}-\frac{1}{cx}\left(e^{cx}-e^{-cx}\right)\right\}$$

If we take into account that:

$$\int_0^\pi f(\vartheta)\,d\vartheta = \int_0^{\frac{\pi}{2}}\{f(\vartheta)+f(\pi-\vartheta)\}\,d\vartheta,$$

then we see that instead of taking the above integral between the limits 0 and π we may take twice this integral between 0 and $\frac{\pi}{2}$. Now we may introduce x as new variable, writing:

$$\cos\vartheta = \frac{1}{\sqrt{3}}\sqrt{x^2-1},\text{ and therefore } -\sin\vartheta\,d\vartheta = \frac{1}{\sqrt{3}}\frac{x\,dx}{\sqrt{x^2-1}},$$

making use of the following series:

$$e^{cx}+e^{-cx}-\frac{1}{cx}\left(e^{cx}-e^{-cx}\right) = 4\left\{\frac{c^2x^2}{3!}+\frac{2c^4x^4}{5!}+\frac{3c^6x^6}{7!}\;\ldots\right\}$$

we find:

$$E = -\frac{2t}{\sqrt{3}}\int_1^2 \frac{x\,dx}{\sqrt{x^2-1}}\left\{\frac{c^2x^2}{3!}+\frac{2c^4x^4}{5!}+\frac{3c^6x^6}{7!}+\ldots\right\}$$

$$= -\frac{t}{\sqrt{3}}\int_1^4 \frac{dy}{\sqrt{y-1}}\left\{\frac{c^2y}{3!}+\frac{2c^4y^2}{5!}+\frac{3c^6y^3}{7!}+\ldots\right\}$$

---

[1] I am indebted for the reduction of this integral to Prof. Dr. W. Kapteyn from Utrecht, to whom I gladly express my thanks for his kind assistance.

If again we substitute $\sqrt{y-1} = z$ then the different terms assume the following form:

$$\int_1^4 \frac{y^k dy}{\sqrt{y-1}} = 2\int_0^{\sqrt{3}} (1+z^2)^k \, dz =$$

$$= 2\sqrt{3}\left\{1 + k\frac{3}{3} + \frac{k(k-1)}{2!}\frac{3^2}{5} + \frac{k(k-1)(k-2)}{3!}\frac{3^3}{7} + \dots\right\}$$

So we find for E a series of the following form:

$$E = -\frac{tc^2}{\sqrt{3}}\left\{\frac{p_1}{3!} + \frac{2c^3}{5!}p_2 + \frac{3c^4}{7!}p_3 + \dots\right\}$$

the coefficients p having the following values:

$$p_1 = 2\sqrt{3}.2$$

$$p_2 = 2\sqrt{3}\,\frac{2^2 \,.\, 6}{5}$$

$$p_3 = 2\sqrt{3}\,\frac{4^2 \,.\, 29}{5 \,.\, 7}$$

$$p_4 = 2\sqrt{3}\,\frac{6^2 \,.\, 602}{5 \,.\, 7 \,.\, 9}$$

$$p_5 = 2\sqrt{3}\,\frac{8^2 \,.\, 70\;0}{5 \,.\, 7 \,.\, 9 \,.\, 11}$$

In order to investigate whether this series converges or not, we notice that in $\int_1^4 \frac{y^k dy}{\sqrt{y-1}}$ the factor $\sqrt{y-1}$ is always positive between the limits 1 and 4. So the value of the integral lies between the values: $y'_k\int_1^4 \frac{dy}{\sqrt{y-1}}$ and $y''_k\int_1^4 \frac{dy}{\sqrt{y-1}}$ where y' represents the minimum value and y'' the maximum value of y between the given limits. Here we have $y' = 1$ and $y'' = 4$. The value of the term of order k of the series for E lies therefore between the terms of order k of the two series:

$$E' = -2t\left\{\frac{c^2}{3!} + \frac{2c^4}{5!} + \frac{3c^6}{7!} \dots\right\}$$

and

$$E' = -2t\left\{\frac{(2c)^2}{3!} + \frac{2\,.\,(2c)^4}{3!} + \frac{3\,.\,(2c)^6}{7!} \dots\right\}$$

and as the ratio between two consecutive terms of these series verges for terms of high degree to zero, the series for E will also converge.

Having determined the value of E, we find the law of attraction by changing the sign and differentiating with respect to r. Of course we must first replace c by $\frac{m^2}{3r^3 t}$. The value which we find for the force is negative; this indicates that the force represents an attraction, as we knew beforehand that we should find. The lowest degree of $1/r$ which occurs in the series is the seventh degree, therefore the force will vary more rapidly than proportional to $\frac{1}{r^7}$.

In connection with this result I wish to make the following remarks.

1st The law for the attraction which we should find on the supposition of vibrating double points whose distance is small compared with the wave length, will probably not differ very much from the law established here, though this question cannot as yet be answered with certainty.

2nd If we assume that m, without being periodical can yet increase or decrease under the influence of $\mathfrak{E}$, then we find a still more rapid variation with r.

Also if we assume that the molecules are not simple double points but more complex configurations, quadruple or octuple points for instance, we find a more rapid variation with r. The double points assumed here seem to yield the slowest variation with r that we can find when we interpret the molecular forces by means of equal positive and negative electrical charges in the molecules. Much sooner, therefore, than to assert that the electron-theory supports the supposition of a molecular attraction proportional to $\frac{1}{r^4}$ we are justified in declaring that this supposition is excluded by the electron-theory.

3rd. If we assume m to be independent of the temperature T, then the attraction which we find, does, indeed, depend upon the temperature and that in such a way that at increasing temperature it decreases more rapidly than $\frac{1}{T}$. We have, however, no reason for supposing m to be independent of T; moreover it makes here an enormous difference whether we are dealing with constant or with vibrating double points. It is therefore impossible to say whether the electric explanation of the molecular forces justifies us in assuming the attraction to increase or to decrease with T.

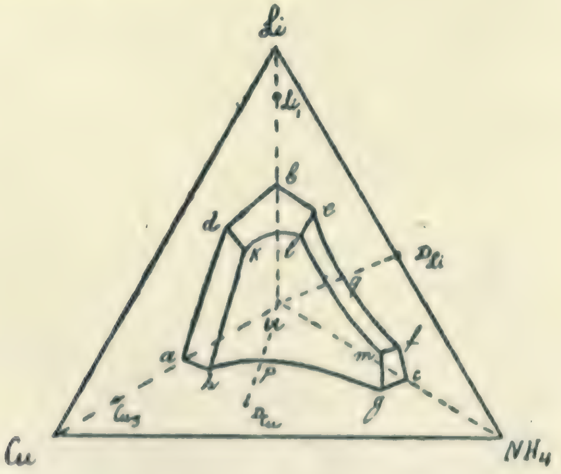
4th. We may wish to determine the shape of the equation of state which follows from the here assumed suppositions as to the action of the molecular forces. If we then follow the virial-method the virial of the resulting mean molecular attraction need only be taken into account. It is true that the molecules exercise on each other still other forces besides this mean attraction, but these forces yield a virial zero. The forces normal to the radius vector, namely form together a couple, and the virial of a couple is zero. For the same reason the directing couples working on the molecules need not be taken into account. And from the forces working in the direction of the radius vector we need only take into account the average value, for attracting and repulsing forces which equally often occur between different pairs of molecules, cancel each other.

In calculating the virial, the influence of the molecular attraction on the distribution in space of the molecules must of course still be taken into account.

Chemistry. — "*Equilibria in quaternary systems.*" By Prof. Dr. F. A. H. Schreinemakers.

In the system: Copper sulphate, ammonium sulphate, lithium sulphate and water two more solid compounds occur at 30° in addition to the three sulphates namely, $Cu\,SO_4\,(NH_4)_2\,SO_4, 6\,H_2O$ and $Li_2\,SO_4\,(NH_4)_2\,SO_4$.

We will again represent the equilibria in the wellknown manner with the aid of a tetrahedron but now choose quite a different projection than that used in the previous communication; we will in fact project all saturation lines and surfaces perpendicularly on one of the side planes of the tetrahedron.



A projection of this kind is represented in the figure; the points

Cu, Li, NH_4 and W indicate the four components $Cu SO_4$, $Li_2 SO_4$, $(NH_4)_2 SO_4$ and water; the triangle Cu Li NH_4 is the side plane on which all is projected. The dotted lines Cu W, Li W and NH_4 W are the projections of the rising sides of the tetrahedron and it is obvious that the point W must lie in the centre of the triangle.

The question is now what connection exists between the position of a point in the tetrahedron and its projection on the triangle Cu Li NH_4.

Let us take a phase with the composition: Cu proportions of $Cu SO_4$, Li proportions of $Li_2 SO_4$, N proportions of $(NH_4)_2 SO_4$ and W proportions of water. The projection of this point on the triangle Cu Li NH_4 may then be taken as indicating a phase which only contains the three components $Cu SO_4$, $Li_2 SO_4$ and $(NH_4)_2 SO_4$.

Let us call these proportions Cu′, Li′ and N′. It is now easily demonstrated that

$$Cu' = Cu + \frac{W}{3} \qquad Li' = Li + \frac{W}{3} \qquad N' = N + \frac{W}{3}$$

so that if the composition of a phase is known its projection may be readily represented in a drawing.

The double salt $Li_2 SO_4 . (NH_4)_2 SO_4$ is represented in the figure by D_{Li}; it is obvious that it must be situated on the line Li NH_4 as it consists merely of the components $Li_2 SO_4$ and $(NH_4)_2 SO_4$. The double salt $Cu SO_4 . (NH_4)_2 SO_4 . 6 H_2 O$ which contains three components must lie on the side plane W Cu NH_4 and is represented by D_{Cu}.

Both copper and lithium sulphate occur as hydrates, namely $Cu SO_4 . 5 H_2 O$ and $Li_2 SO_4 . H_2 O$; they are represented in the figure by Cu_5 and Li_1; of course Cu_5 must lie on the side Cu W and Li on Li W.

Let us first consider the three ternary equilibria.

1. *Copper sulphate—ammonium sulphate—water.* The equilibria occurring in this system at 30° have been determined by Miss W. C. DE BAAT; the results of this investigation are represented by the saturation lines *a h*, *h p g*, and *g c*; *ah* indicates the solutions saturated with $Cu SO_4 . 5 H_2 O$; *g c* is the saturation line of solid $(NH_4)_2 SO_4$ and *h p g* represents the solutions saturated with $Cu SO_4$ $(NH_4)_2 SO_4 . 6 H_2 O$. As the line W D_{Cu} intersects the saturation line *h p g*, the double salt is soluble in water without decomposition; its solubility is represented by *p*.

2. *Lithium sulphate—ammonium sulphate—water.* The equilibria occurring in this system at 30° are represented by the saturation lines *b e*, *e q f* and *f c*; the first is the saturation line of $Li_2 SO_4 . H_2 O$;

the second that of the double salt $Li_2\,SO_4 . (NH_4)_2\,SO_4$, the last that of $(NH_4)_2\,SO_4$. As the line W D_{Li} intersects the saturation line of the double salt it is soluble in water without decomposition.

As regards the branch *be* I stated that this indicates solutions which are in equilibrium with $Li_2\,SO_4 . H_2O$; this is not quite correct for lithium sulphate, although only to the extent of a few $^0/_0$, gives mixed crystals with ammonium sulphate.

3. *Lithium sulphate—copper sulphate—water.* Whereas in the two previous ternary systems a double salt occurs, this is not the case in this system at 30°; the isotherm therefore only consists of two branches; *ad* is the saturation line of $Cu\,SO_4\ 5\,H_2O$ and *bd* that of $Li_2\,SO_4 . H_2O$.

These two branches have been determined by Mr. KOOPAL.

The quaternary equilibria at 30° are represented by surfaces, lines and points.

The surface *ahkd* is the saturation surface of $Cu\,SO_4, 5\,H_2O$; it therefore indicates the quaternary solutions which are saturated with $Cu\,SO_4 . 5\,H_2O$.

The surface *dkleb* is the saturation surface of $Li_2\,SO_4 . H_2O$.

The surface *cfmg* is the saturation surface of $(NH_4)_2\,SO_4$.

The three surfaces observed are the saturation surfaces of the components or of their hydrates; in addition we also have the saturation surfaces of the double salts; that of $Li_2\,SO_4 . (NH_4)_2\,SO_4$ is represented by *elmfq*; that of $Cu\,SO_4 . (NH_4)_2\,SO_4 . 6\,H_2O$ by *hklmgph*.

The saturation lines are formed by the intersection of the saturation surfaces taken two by two; they consequently represent solutions saturated with two solid substances.

We now see at once that solutions represented by the points of the lines:

hk are saturated with $Cu\,SO_4 . 5\,H_2O$ and D_{Cu}
dk „ „ „ $Cu\,SO_4 . 5\,H_2O$ and $Li_2\,SO_4 . H_2O$
kl „ „ „ $Li_2\,SO_4 . H_2O$ and D_{Cu}
le „ „ „ $Li_2\,SO_4 . H_2O$ and D_{Li}
lm „ „ „ D_{Li} and D_{Cu}
mf „ „ „ D_{Li} and $(NH_4)_2\,SO_4$
mg „ „ „ D_{Cu} and $(NH_4)_2\,SO_4$

The quaternary saturation lines may be distinguished into external lines and middle lines; the external lines such as *kh*, *kd*, *le*, *mf* and *mg* each terminate in a point of a side plane, therefore in a ternary solution; the middle lines such as *kl* and *lm* are situated quite within the tetrahedron.

In each of the saturation points three saturation surfaces and therefore also three saturation lines meet each other; such a point therefore represents a solution saturated with three solid substances.

From this it follows that the solution represented:

by *k* is saturated with $Cu\,SO_4 . 5\,H_2O$, $Li_2\,SO_4 . H_2O$ and D_{Cu}
„ *l* „ „ „ D_{Li}, $Li_2\,SO_4 . H_2O$ and D_{Cu}
„ *m* „ „ „ D_{Li}, $(NH_4)_2\,SO_4$ and D_{Cu}.

This shows that each of these solutions is saturated with $Cu\,SO_4 . (NH_4)_2\,SO_4 . 6\,H_2O$.

With the aid of this figure we may readily draw some conclusions. Let us therefore observe the external lines, for instance *dk*. The point *d* represents a ternary solution saturated at 30° with $Cu\,SO_4 . 5\,H_2O$ and $Li_2\,SO_4 . H_2O$. To this solution we add $(NH_4)_2\,SO_4$; the solution will now alter its composition until at last a third solid phase appears. What is this phase? $(NH_4)_2\,SO_4$ forms a double salt with copper as well as with lithium sulphate and the question now arises which of these two will appear first. The experiment shows that $Cu\,SO_4 . (NH_4)_2SO . 6\,H_2O$ is formed. If we start from the ternary solution *h* which is saturated at 30° with $Cu\,SO_4 . 5\,H_2O$ and $Cu\,SO_4 . (NH_4)_2\,SO_4 . 6\,H_2O$ and if $Li_2\,SO_4 . H_2O$ is added the solution undergoes the changes represented by points of the line *hk* until finally the third solid phase occurs in *k* in this case $Li_2\,SO_4 . H_2O$.

If we start from the ternary solution *f* saturated at 30° with $(NH_4)_2\,SO_4$ and $Li_2\,SO_4 . (NH_4)_2\,SO_4$ and if we add $Cu\,SO_4 . 5\,H_2O$ and represent the solution by *m* $Cu\,SO_4 . (NH_4)_2\,SO_4 . 6\,H_2O$ is formed as the third solid phase; if we start from the ternary solution *g* which is saturated with $(NH_4)_2\,SO_4$ and $Cu\,SO_4 . (NH_4)_2\,SO_4 . 6\,H_2O$ and add $Li_2\,SO_4 . H_2O$, $Li_2\,SO_4 . (NH_4)_2\,SO_4$ will form in *m* as the third phase.

If we start from the ternary solution *e* which is saturated with $Li_2\,SO_4 . H_2O$ and $Li_2\,SO_4 . (NH_4)_2\,SO_4$ and add $Cu\,SO_4 . 5\,H_2O$ the solution traverses the branch *el*; in *l* however a new solid phase is formed, namely, $Cu\,SO_4 . (NH_4)_2\,SO_4 . 6\,H_2O$.

Suppose a plane is passed through the points W, Cu and D_{Li} of the tetrahedron; the points of this plane represent solutions with a constant proportion of the components $Li_2\,SO_4$ and $(NH_4)_2\,SO_4$; this ratio is the same as that in which they occur in the double salt. This plane intersects the saturation surface *leqfm* of this double salt, so that this is not only soluble without decomposition in water but also in solutions of copper sulphate of a definite concentration.

In order to find the composition of the solid phases which can be in equilibrium with definite solutions I have acted in the same manner as I did previously with ternary systems; I have applied the "residue-method".

If the solution is in equilibrium with one solid substance the conjugation line solution-residue must pass through the point indicating this solid substance; if it is in equilibrium with two solid substances the conjugation line solution-residue intersects the communication line of the two solid substances and if it is in equilibrium with three solid substances it intersects the triangle which has those three solid substances as its angular points.

These constructions are much facilitated by taking a rectangular tetrahedron instead of an equilateral one and projecting the whole on two of the side planes.

Astronomy. — "*The investigation of the weights in equations according to the principle of the least squares*". By J. WEEDER. (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN).

When results of measurement deduced from different modes of measuring or originating from different observers are equated mutually, it is generally advisable to test the weights assigned to these results, before equating, with the apparent errors produced by the equation in order to be able to judge whether it is necessary to correct them and to distinguish in what direction correction is obtained. Let the material of observation break up according to its origin into groups and let out of the apparent errors of each group separately the mean error of the unity of weight be deduced, then it is a necessity for the differences of those values to be small, at least they may not overstep the limits which can be fixed taking into account the numbers of apparent errors in each group.

Already at the outset of such investigations the problem thus appears how the mean error of the unity of weight can be calculated, if one wishes to use but a part of the apparent errors.

When equating determinations of errors of division of the Leyden meridian circle I have applied the following formula:

$$\mu = \sqrt{\frac{\Sigma g f^2}{n-k}}.$$

Here

μ = the mean error of unity of weight,

g = the weight of a result of observation,

$f =$ the apparent error calculated for this result,
$n =$ the number of errors out of the group,
$k =$ a number depending on the weights of the results of measurement and on the coefficients the unknown quantities, determined by the equating, are associated with in the equations expressing the connection between these unknown quantities and the results of measurement of the group.

In what way k is dependent on the above-mentioned quantities will become clear by an example for which I choose the case that 3 unknown quantities x, y, z are determined by N equations of the form $ax + by + cz = l$, whilst to the quantities l appearing in this equation and obtained by measurement the weights g are due. In this case

$$k = \Sigma\, g\,(a^2\, Q_{xx} + 2ab\, Q_{xy} + b^2\, Q_{yy} + 2ac\, Q_{xz} + 2bc\, Q_{yz} + c^2\, Q_{zz})$$

where the summations in the formulae for k and μ include expressions relating to the same results of measuring. In the above formula the quantities Q, the well-known numbers of weight, can be calculated by means of the coefficients of the normalequations.

For the deduction of this formula we have the same considerations which lead to the mean error of the unity of weight out af *all* observations. If the real errors are indicated by h then $n\mu^2 = \Sigma\, gh^2$; this sum is expressed in the apparent errors that can be calculated, and in the errors Δx, Δy and Δz of the quantities x, y and z, calculated out of the normal equations, by means of the relation $h = f + a\Delta x + b\Delta y + c\Delta z$, so that

$$\begin{aligned} n\mu^2 = {} & \Sigma\, gf^2 + 2\,(\Delta x\, \Sigma\, gfa + \Delta y\, \Sigma\, gfb + \Delta z\, \Sigma\, gfc) + \\ & + (\Delta x)^2\, \Sigma\, ga^2 + 2\,(\Delta x)\,(\Delta y)\, \Sigma'\, gab + (\Delta y)^2\, \Sigma'\, gb^2 + \\ & + 2\,(\Delta x)\,(\Delta z)\, \Sigma\, gac + 2\,(\Delta y)\,(\Delta z)\, \Sigma\, gbc + (\Delta z)^2\, \Sigma\, gc^2 \end{aligned}$$

If we were to use the whole material of errors, then the first three of the unknown terms would fall out on account of $[gfa] = 0$, $[gfb] = 0$ and $[gfc] = 0$. (Here and for the future I make use of $[\,]$ as sign of a summation extending over *all* observations). To take as well as possible the unknown terms in the above into account we replace them by their mean values in the supposition that the same complex of observations repeats itself manifold times so that all calculable quantities return unmodified in each repetition. In that supposition Δx, Δy and Δz have zero as mean values and the mean values of their squares and products are in the above order:

$$Q_{xx}\,\mu^2 \;,\; Q_{xy}\,\mu^2 \;,\; Q_{yy}\,\mu^2 \;,\; Q_{xz}\,\mu^2 \;,\; Q_{yz}\,\mu^2 \text{ and } Q_{zz}\,\mu^2$$

If we connect these mean values having μ^2 as factor with the term

$n\mu^2$ in the above equation, if we put

$$\Sigma\, g\,(a^2 Qxx + 2abQxy + b^2 Qyy + 2acQxz + 2bcQyz + c^2 Qzz),$$

equal to k and if we solve μ out of the equation, we obtain $\mu = \sqrt{\dfrac{\Sigma g f^2}{n-k}}$, i. e. the formula of which I made use to determine the mean error of the unity of weight out of a particular group of apparent errors.

I arrived at *about* the same result by another consideration putting to myself the problem to determine the mean value M_{fi} of a definite apparent error f_i. In the relation :

$$f_i = l_i - a_i\, x - b_i\, y - c_i\, z$$

I substituted for x, y, z respectively $[\alpha l]$, $[\beta l]$, $[\gamma l]$ to obtain f_i in the form of a linear expression of the results of measuring l which are supposed to be quite independent of each other.

Then :

$$M^2{}_{fi} = \left\{ 1 - 2\,(a_i\,\alpha_i + b_i\,\beta_i + c_i\,\gamma_i\,) \right\} \frac{\mu^2}{g_i} + \left[(a_i\,\alpha + b_i\,\beta + c_i\,\gamma)^2 \frac{\mu^2}{g} \right].$$

It would now be the only way of reduction of this equation to make use of the well-known relations existing between the coefficients α, β, γ and a, b, c and the numbers of weight Q, namely :

$$\alpha = g\,(a\,Qxx + b\,Qxy + c\,Qxz)\,,$$
$$\beta = g\,(a\,Qxy + b\,Qyy + c\,Qyz)\,,$$
$$\gamma = g\,(a\,Qxz + b\,Qyz + c\,Qzz)\,,$$

in order to prove that

$$\left[a_i\,\alpha + b_i\,\beta + c_i\,\gamma)^2 \frac{1}{g} \right] = \frac{a_i\,\alpha_i + b_i\,\beta_i + c_i\,\gamma_i}{g_i}\,.$$

I propose however to deduce this equation directly from the minimum condition :

$$[g\,(l - ax - by - cz)^2] = \text{minimum}.$$

If here too x, y, z are replaced by $[\alpha l]$, $[\beta l]$ and $[\gamma l]$, then after calculation and combination of the equal powers and products of the quantities l an expression appears of the form $\Sigma\,\Sigma\, C_\mu^\nu\, l_\mu\, l_\nu$, having for the right set of coefficients α, β, γ a minimum value. I observe here that the coefficients α, β, γ have to satisfy the minimum condition independently of the particular values which the measurements furnished for the quantities l. Out of this observation ensues that the partial derivatives of C_μ^ν with respect to each of the coefficients α, β, γ furnish zero by substitution of the right values of these coefficients.

By calculation and arrangement of the terms of the minimum condition we arrive at

$$C^{\nu}_{\mu} = 2\,[g\,(a\alpha_{\mu} + b\beta_{\mu} + c\gamma_{\mu})(a\alpha_{\nu} + b\beta_{\nu} + c\gamma_{\nu})] -$$
$$- 2\,g_{\mu}\,(a_{\mu}\alpha_{\nu} + b_{\mu}\beta_{\nu} + c_{\mu}\gamma_{\nu}) - 2\,g_{\nu}\,(a_{\nu}\alpha_{\mu} + b_{\nu}\beta_{\mu} + c_{\nu}\gamma_{\mu})$$

The expression $[g\,(a\,\alpha_{\mu} + b\,\beta_{\mu} + c\,\gamma_{\mu})\,(a\,\alpha_{\nu} + b\,\beta_{\nu} + c\,\gamma_{\nu})]$ being put equal to F, the conditions for the minimum furnish the following equations:

$$\frac{\partial F}{\partial \alpha_{\mu}} = g_{\nu}\,a_{\nu}\,\frac{\partial F}{\partial \beta_{\mu}} = g_{\nu}\,b_{\nu}\,\frac{\partial F}{\partial \gamma_{\mu}} = g_{\nu}\,c_{\nu},$$
$$\frac{\partial F}{\partial \alpha_{\nu}} = g_{\mu}a_{\mu}\frac{\partial F}{\partial \beta_{\nu}} = g_{\mu}b_{\mu}\frac{\partial F}{\partial \gamma_{\nu}} = g_{\mu}c_{\mu}.$$

Such an expression F which, as far as the coefficients α, β, γ appear in it, contains only products of one of the $\alpha_{\mu}\,\beta_{\mu}\,\gamma_{\mu}$ with *one* of the $\alpha_{\nu}\,\beta_{\nu}\,\gamma_{\nu}$ can be written as linear expression in each of those sets of 3 coefficients in the following way:

$$F = \alpha_{\mu}\frac{\partial F}{\partial \alpha_{\mu}} + \beta_{\mu}\frac{\partial F}{\partial \beta_{\mu}} + \gamma_{\mu}\,\frac{\partial F}{\partial \gamma_{\mu}} = \alpha_{\nu}\,\frac{\partial F}{\partial \alpha_{\nu}} + \beta_{\nu}\frac{\partial F}{\partial \beta_{\nu}} + \gamma_{\nu}\,\frac{\partial F}{\partial \gamma_{\nu}}.$$

So that by substituting the equations resulting from the minimum we arrive at the following relations:

$$F = g_{\nu}\,(a_{\nu}\,\alpha_{\mu} + b_{\nu}\,\beta_{\mu} + c_{\nu}\,\gamma_{\mu}) = g_{\mu}\,(a_{\mu}\,\alpha_{\nu} + b_{\mu}\,\beta_{\nu} + c_{\mu}\,\gamma_{\nu}).$$

In words this relation runs: with equal weights an error in l_{μ} has equal influence on the apparent error f_{ν} as an equally large error in l_{ν} has on the apparent error f_{μ}. If the weights of the two results of measuring are unequal, errors in these which are in inverse ratio with their weights will cause each other's apparent errors to deviate to the same amount from the true ones.

Let us put in the condition

$$[g\,\{l - a\,[\alpha l] - b\,[\beta l]\ - c\,[\gamma l]\,\}^2] = \text{minimum}$$

$l_i = 1$ and all other quantities $l = 0$, then from this arises

$$g_i\ (1 - 2a_i\alpha_i - 2b_i\beta_i - 2c_i\gamma_i) + [g\ (a\alpha_i + b\beta_i + c\gamma_i)^2] = \text{min.}$$

from which we deduce putting $[g\,(a\alpha_i + b\beta_i + c\gamma_i)^2] = G$:

$$\frac{\partial G}{\partial \alpha_i} = 2g_i a_i\,\frac{\partial G}{\partial \beta_i} = 2g_i b_i\,\frac{\partial G}{\partial \gamma_i} = 2g_i c_i$$

and from this ensues again:

$$G = \frac{1}{2}\,\alpha_i\,\frac{\partial G}{\partial \alpha_i} + \frac{1}{2}\,\beta_i\,\frac{\partial G}{\partial \beta_i} + \frac{1}{2}\,\gamma_i\,\frac{\partial G}{\partial \gamma_i} = g_i\,(a_i\alpha_i + b_i\beta_i + c_i\gamma_i).$$

With the aid of the above deduced theorem each term of the summation in the expression $[g\,(a\alpha_i + b\,\beta_i + c\,\gamma_i)^2]$ can be replaced by a corresponding one in which the constant index i is given to the coefficients a, b, c, so we have:

$$G = \left[\frac{g_i^2}{g}(a_i\,\alpha + b_i\,\beta + c_i\,\gamma)^2\right] = g_i\,(a_i\,\alpha_i + b_i\,\beta_i + c_i\,\gamma_i)$$

from which results after division by g_i^2 the relation I was to prove.

Using this relation I find:

$$M_{fi}^2 = (1 - a_i\,\alpha_i - b_i\,\beta_i - c_i\,\gamma_i)\,\frac{\mu^2}{g_i}.$$

If we call $a\,\alpha + b\,\beta + c\gamma = \varkappa$, then $f\sqrt{\dfrac{g}{1-\varkappa}}$ can be calculated out of each apparent error and the mean value of this system of errors is equal to μ, as that of the system of unknown errors is $h\sqrt{g}$. It therefore seems to me not only permissible, but for a test of the weights even useful, to make use of that system of errors which allows the mean error of the unity of weight to be deduced out of each definite part of these errors. The connection between the quantities $\varkappa$ and the number k of the above formula applied by me can be indicated by the relation $\Sigma\,\varkappa = k$.

Physics. - "*Contribution to the theory of binary mixtures*". VII.

By Prof. J. D. VAN DER WAALS.

ON THE RELATION BETWEEN THE QUANTITIES a_{12} AND a_1 AND a_2, WHICH OCCUR IN THE THEORY OF A BINARY MIXTURE.

I have already frequently traced the course of the thermodynamic curves for the case that for a binary system minimum plaitpoint temperature occurs, and so also the quantity $\frac{a_x}{b_x}$ has a minimum value for certain value of x. Both the course of the isobars and the course of the lines $\left(\frac{dp}{dx}\right)_v = 0$ and $\left(\frac{dp}{dv}\right)_x = 0$ may be assumed as known for that case. And experiment has shown that the shape of these lines predicted by theory it at least qualitatively accurate.

I purpose to demonstrate in these pages that in the case mentioned the course of these lines (see among others fig. 1 page 626 Vol. IX of these Proceedings 1907) is not compatible with the supposition $a_{12}^2 = a_1\,a_2$.

I begin with pointing out that the line $\left(\frac{dp}{dx}\right)_v = 0$ has an asymptote for such a value of x for which $MRT\frac{db}{dx} = \frac{da}{dx}$, which asymptote either exists or must be supposed to exist for a value of x which is negative, and that this curve approaches the line $v = b$ asymptotically for continually increasing values of x — at least if $a_1 + a_2 - 2a_{12}$ is positive. I shall presently come back to this supposition, but on page 626 I have explicitly stated this supposition in the form $\frac{d^2a}{dx^2}$ positive. With increase of T this line proceeds to higher value of x and v.

At lower temperatures the line $\left(\frac{dp}{dv}\right)_x = 0$ consists of two separate branches. From $\frac{d^2p}{dv^2}\frac{dv}{dx} + \frac{d^2p}{dx\,dv} = 0$ follows that the liquid branch has maximum volume on the line $\frac{d^2p}{dx\,dv} = 0$ and the vapour branch minimum volume on the same curve, which curve has an analogous course to $\left(\frac{dp}{dx}\right) = 0$. It has the same asymptotes, but is always confined to greater volume. For $T =$ minimum critical temperature the two branches coincide in a point for which both $\frac{d^2p}{dv^2}$ and $\frac{d^2p}{dx\,dv}$ is equal to 0, so in such a point of the line $\frac{d^2p}{dx\,dv} = 0$, for which $\left(\frac{dp}{dv}\right)_x = 0$ and also $\frac{d^2p}{dv^2} = 0$. Hence in the critical point of the mixture taken as homogenous, for which $\frac{a_x}{b_x}$ has minimum value. At still higher value of T the curve $\left(\frac{dp}{dv}\right)_x = 0$ has split up into a lefthand branch and a righthand branch, both which branches possess tangents parallel to the v-axis, in points for which also $\left(\frac{dp}{dv}\right)_x = 0$ and $\frac{d^2p}{dv^2} = 0$. Among the special values of this constantly increasing value of T we must mention in the first place that for which the last mentioned point has got on the line $\left(\frac{dp}{dx}\right)_v = 0$, the point P of fig. 31. This is the

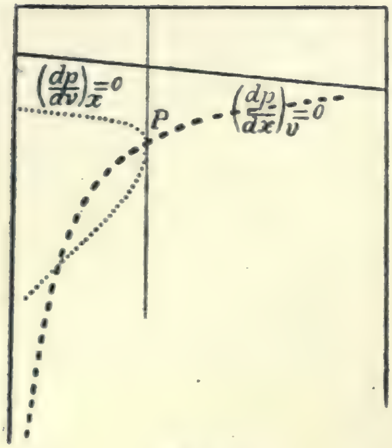

$\left(\frac{dp}{dv}\right)_x=0$
P
$\left(\frac{dp}{dx}\right)_v=0$

Fig. 31.

remarkable point for which *plaitpoint* and *critical point of the mixture* taken as homogeneous coincide. So at this temperature the two curves $\left(\frac{dp}{dx}\right)_v = 0$ and $\left(\frac{dp}{dv}\right)_x = 0$ still intersect in two points. The other point of intersection lies, of course, at greater volume. With further rise of temperature the two curves contract further. The line $\left(\frac{dp}{dx}\right)_v = 0$ moves to the right and the line $\left(\frac{dp}{dv}\right)_x = 0$ to the left. At a certain temperature these two curves touch, and at still higher temperature they have got quite detached. This point of contact of the two curves lies, of course, on the vapour branch of $\left(\frac{dp}{dv}\right)_x = 0$, and so has a greater volume than the critical volume.

We can calculate the volume in case of contact. The condition of contact of $\left(\frac{dp}{dv}\right)_x = 0$ and $\left(\frac{dp}{dx}\right)_v = 0$ is given by equal value of $\frac{dv}{dx}$ in the two following equations:

$$\frac{d^2p}{dv^2}\frac{dv}{dx} + \frac{d^2p}{dxdv} = 0$$

and

$$\frac{d^2p}{dxdv}\frac{dv}{dx} + \frac{d^2p}{dx^2} = 0$$

or from:

$$\frac{d^2p}{dv^2}\frac{d^2p}{dx^2} = \left(\frac{d^2p}{dxdv}\right)^2 \quad \text{(see p. 691).}$$

This latter equation and the two equations $\left(\frac{dp}{dx}\right)_v = 0$ and $\left(\frac{dp}{dv}\right) = 0$ form a set of three which is sufficient for the determination of the three quantities x, v and T of the point of contact. If we assume b to be constant in the equation of state these equations have the following form:

$$\left[\frac{MRT}{(v-b)^3} - \frac{3a}{v^4}\right]\left[\frac{MRT\left(\frac{db}{dx}\right)^2}{(v-b)^3} - \frac{1}{2}\frac{\frac{d^2a}{dx^2}}{v^3}\right] = \left[\frac{MRT\frac{db}{dx}}{(v-b)^2} - \frac{\frac{da}{dx}}{v^2}\right]^2 \quad . \quad . \quad . \quad (1)$$

$$\frac{MRT}{(v-b)^2}\frac{db}{dx}=\frac{da}{dx}\frac{1}{v^2} \quad \dots \dots \dots \quad (2)$$

and

$$\frac{MRT}{(v-b)^2}=\frac{2a}{v^3} \quad \dots \dots \dots \quad (3)$$

If now we make use of (2) and (3) for the elimination of MRT and of $\frac{db}{dx}$, we get a simple form for $\frac{v}{b}$, viz.:

$$\frac{v}{b}=\frac{3a\frac{d^2a}{dx^2}-2\left(\frac{da}{dx}\right)^2}{a\frac{d^2a}{dx^2}-\left(\frac{da}{dx}\right)^2} \quad \dots \dots \dots \quad (4)$$

We may also get a quadratic equation in $\frac{v}{b}$, but then it appears that one of the values of $\frac{v}{b}=1$, and that at $T=0$ the line $v=b$ may be considered as coinciding with the branch of the volumes of $\left(\frac{dp}{dv}\right)_x=0$, and also with $\left(\frac{dp}{dx}\right)_v=0$. In the same way the line $v=\infty$.

If we now write for the ratio of $\left(\frac{da}{dx}\right)^2$ and $a\frac{d^2a}{dx^2}$ the quantity m, so that $m=\frac{\left(\frac{da}{dx}\right)^2}{a\frac{d^2a}{dx^2}}$ then (4) becomes:

$$\frac{v}{b}=\frac{3-2m}{1-m}.$$

And drawing $\frac{v}{b}$ as ordinate when m is laid out along the axis of the abscissae, we get fig. 32. For $m=0$ we have $\frac{v}{b}=3$ and for $m=1$ we have $\frac{v}{b}=\infty$. For $m>1$ $\frac{v}{b}$ is at first negative, but for $m={}^3/_2$ $\frac{v}{b}=0$, and for greater values of m $\frac{v}{b}$ is positive and steadily increasing. The limiting value is $\frac{v}{b}=2$. For negative value of m $\frac{v}{b}$ is always positive, descending from $\frac{v}{b}=3$ to $\frac{v}{b}=2$. The traced curve is an equilateral hyperbola. So a value of $\frac{v}{b}$ larger than 3 is possible only when v lies between 0 and 1. Thus $\frac{v}{b} = 4$ requires a value of $m = {}^1/_2$.

Accordingly it is impossible to account for a minimum plaitpoint temperature of substances for which m does not lie between 0 and 1.

Now I have already repeatedly called attention to the equation:

$$2a \frac{d^2a}{dx^2} = \left(\frac{da}{dx}\right)^2 + 4\,(a_1a_2 - a_{12}^2),$$

which follows from the supposition that a is a quadratic form of x, and already in my Molecular Theory for a binary mixture I pointed out, realizing the desirability of a relation being found between a_{12} and a_1 and a_2, that the equation of the spinodal line for a binary mixture might be very much simplified if we were justified in assuming $a_{12}^2 = a_1\,a_2$. I also pointed out other relations between these quantities; but I have carefully refrained from even giving so much as the slightest indication of the greater probability of one relation. I have only repeatedly, then and later, assumed as relation for mixtures with minimum plaitpoint temperature $a_1 + a_2 > 2a_{12}$, and reversely, when also mixtures with maximum plaitpoint temperature might occur: $a_1 + a_2 < 2a_{12}$. And I have repeatedly pointed out that there is no reason whatever for putting e. g. $a_{12}^2 = a_1a_2$. And to this the following considerations have chiefly led me.

In the equation of state for a simple substance the two constants b and a have not been introduced on equally sufficient grounds and with the same certainty. To the existence of the quantity b we conclude with perfect certainty if we believe that to occupy space is an essential property of matter Even MAXWELL, who would not attribute a volume of their own to the molecules, but wanted to consider them as so-called material points, understanding that collisions could not take place between material points, could not but attribute to them at least an apparent volume. By assuming a repulsive force he had to account for their never meeting, and for their behaviour as particles possessing impermeability on approaching each other with reversal of motion. A hypothesis whose improbability is not to be denied. The force would be a repulsive one, and probably in inverse ratio to the fifth power of the distance. How and why the attraction at somewhat larger distance is converted into such a repulsive force is a question that was probably never put by him, and at all events was not answered by him. So the introduction of the quantity b into the equation of state is perfectly natural — and for everybody who assumes the existence of matter as real, indispensable. But this is not, at least not in the same degree, the case with the quantity a. Why should molecular attraction be a necessary attribute of matter? From the idea: "matter is something that necessarily occupies space" does not follow that matter will also have to possess attraction. Perhaps we shall sooner or later learn to form a conception on the nature of a molecule which involves that they necessarily attract each other and learn to compute the value of this attraction. Of late attempts have therefore been made to get a better insight into the nature of molecules, and they are supposed to be either vibrating or permanent electrical double points [1]). But even if this supposition appeared to account satisfactorily for the molecular attraction, yet it does not necessarily follow that attraction exists. Then the question has changed in so far that it runs: are there electrical double points in the molecule or not? It is true that in my Thesis for the Doctorate (1873) p. 92, when the question occurred whether hydrogen possesses a critical temperature I answered in the sense of a high degree of probability, but only on a ground which leaves some room for doubt, viz. that "It may be presumed that matter will always have attraction". It is not to be denied that everything that we accept as matter is subjected to gravity; but to derive from this that the existence of the NEWTONIAN attraction involves the possession of molecular attraction is more than hazardous. All this is not intended to raise doubt about the existence of a e. g. for helium, for now that all other substances possess a value for a we may repeat what I said before for hydrogen, but to draw attention to the fact that the value of a does not only depend on the molecular weight. If this *was* the case, $\frac{a_1}{m_1^2} = \frac{a_2}{m_2^2}$, a relation which is certainly not fulfilled. Then also $\frac{a_1}{m_1^2} = \frac{a_2}{m_2^2} = \frac{a_{12}}{m_1 m_2}$, and $a_{12}^2 = a_1 a_2$ which very probably will never be fulfilled either.

I was convinced from the outset that we should not be able to explain a number of phenomena occurring for binary mixtures by means of such an unfounded supposition. Already a long time ago KORTEWEG showed in his paper "La surface ψ dans le cas de symétrie" in how high a degree the phenomena exhibited by a binary mixture, depend on the value ascribed to a_{12}. For values of a_{12} between certain limits not only three phase equilibrium but even four phase equilibrium would be possible, then of course always at a single value of T. So the supposition $a_{12}^2 = a_1 a_2$ is not one without far-reaching consequences. Yet we see repeatedly that this supposition is made. And I have undertaken this investigation to show that such a supposition would also render the existence of minimum plaitpoint temperature impossible. At the same time I wanted to point out how the course of the isobars which I have given in fig. 1 of these contributions would be entirely modified on other suppositions about a_{12} than those I have started from. If we put in equation:

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[1]) See these Proc. p. 132.

$$2a\frac{d^2a}{dx^2} = \left(\frac{da}{dx}\right)^2 + 4\,(a_1a_2 - a_{12}^2)$$

for $\left(\frac{da}{dx}\right)^2$ the value $ma\frac{d^2a}{dx^2}$ in which, if there is minimum plaitpoint temperature the value of m lies between 0 and 1 for the point of contact of $\left(\frac{dp}{dx}\right)_v = 0$ and $\left(\frac{dp}{dv}\right)_x = 0$, we find:

$$\left(\frac{2}{m} - 1\right)\left(\frac{da}{dx}\right)^2 = 4\,(a_1a_2 - a_{12}^2)$$

$$(2 - m)\,a\frac{d^2a}{dx^2} = 4\,(a_1a_2 - a_{12}^2)$$

Now $\frac{d^2a}{dx^2} = 2\,(a_1 + a_2 - 2a_{12})$. As at the same time we cannot have $a_1a_2 = a_{12}^2$ and $a_1 + a_2 = 2a_{12}$, unless in the case $a_1 = a_2$, this equation cannot be fulfilled but by putting $a_1a_2 > a_{12}^2$.

The supposition $a_1a_2 = a_{12}^2$ gives for m the value 2, but then also for $\frac{v}{b}$ in the point of contact of $\left(\frac{dp}{dx}\right)_v = 0$ and $\left(\frac{dp}{dv}\right)_x = 0$, the value 1 (see fig. 32). — Only when we put $a_1\,a_2 < a_{12}^2$ does m become > 2, and do we find for the point of contact of the curve mentioned, values of $\frac{v}{b}$ which are larger than 1, and which can therefore exist, but then this value can rise to 2 at the utmost. In such cases there is contact of $\left(\frac{dp}{dx}\right)_v = 0$ with the liquid branch of $\left(\frac{dp}{dv}\right)_x = 0$. And this means for fig. 1 of these contributions that then again the liquid branch of $\left(\frac{dp}{dv}\right)_x = 0$ may approach to $\left(\frac{dp}{dx}\right)_v = 0$ on the right side, but then to that part of this curve that lies beyond the minimum

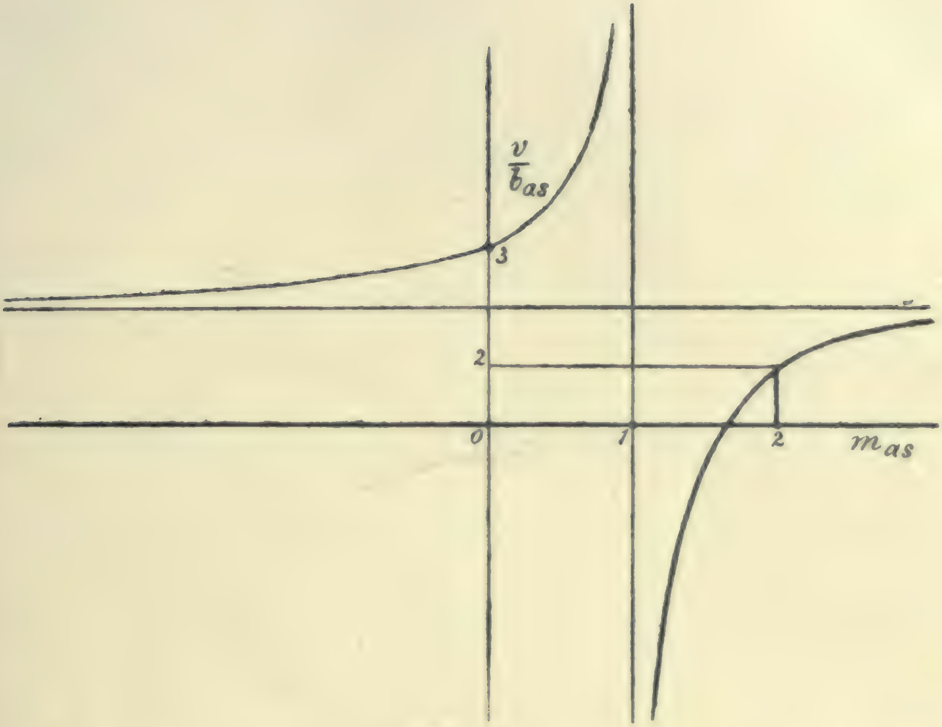

Fig. 32.

volume, and where it proceeds again to greater volumes. On the supposition that a_{12}^2 might rise above $a_1 a_2$, fig. 1 would not represent all possible cases of the course of the isobars with respect to $\left(\frac{dp}{dx}\right)_v = 0$. But I observed already on page 630 in what way fig. 1 would have to be extended if other suppositions on $a_1 + a_2 - 2a_{12}$ are admitted e. g. $a_1 + a_2 - 2a_{12} = 0$ or $a_1 + a_2 - 2a_{12}$ negative, and the supposition $a_1 a_2 < a^2_{12}$ lies in this direction.

If we continue increasing a_{12}, not only above $\sqrt{a_1 a_2}$, but even above $\frac{a_1 + a_2}{2}$, then $m = \frac{\left(\frac{da}{dx}\right)}{a\frac{d^2a}{dx^2}}$ is negative, and $\frac{v}{b}$ lies between 2 and 3 for the point of contact of $\left(\frac{dp}{dx}\right)_v = 0$ and $\left(\frac{dp}{dv}\right)_x = 0$, and so this point of contact always lies on the liquid branch of $\left(\frac{dp}{dv}\right)_x = 0$.

We might also have arrived at the above results by another course, which would give us an opportunity of making some new remarks. For if we think the quantity v eliminated from the two equations

$\left(\frac{dp}{dx}\right)_v = 0$ and $\left(\frac{dp}{dv}\right)_x = 0$, we obtain a relation between x and T. In general we find two values of x for the same value of T. The value of T, at which these values of x coincide, or in other words, the maximum value of T, then gives us the value of x for the point of contact of the two curves.

From

$$\frac{MRT}{(v-b)^2} = \frac{2a}{v^3}$$

and

$$\frac{MRT}{(v-b)^2}\frac{db}{dx} = \frac{1}{v^2}\frac{dv}{dx}$$

we find

$$\frac{2\frac{db}{dx}}{v} = \frac{\frac{da}{dx}}{a} \text{ for a point of intersection.} \quad . \quad (6)$$

As for values of v which will be realisable, $v > b$ and v must be positive, a point of intersection of the two curves can only occur if $\frac{da}{dx}$ is positive, and if $\frac{\frac{da}{dx}}{a} < \frac{2\frac{db}{dx}}{b}$. This latter condition may be written $\frac{d\frac{a}{b^2}}{dx} < 0$. So the two curves can never intersect in a region of increasing critical pressure. Let us therefore confine ourselves to decreasing critical pressure. The locus (6) has as differential equation:

$$-\frac{2\frac{db}{dx}}{v^2}\frac{dv}{dx} = \frac{a\frac{d^2a}{dx^2} - \left(\frac{da}{dx}\right)^2}{a^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

So when $m = \frac{\left(\frac{da}{dx}\right)^2}{a\frac{d^2a}{dx^2}} < 1$, $\frac{dv}{dx}$ is negative. Only in a region where m has become $= 1$, $\frac{dv}{dx}$ will be positive. And if we should assume $a_1 a_2 = a_{12}^2$, so if we put $m = 2$, the locus of the points of intersection of the two curves would move to greater volume with increasing x, so perfectly different from what happens for mixtures with minimum plaitpoint temperature. If we substitute the value of v which follows from (6), in:

$$MRT = \frac{2a}{b}\frac{b}{v}\left(1 - \frac{b}{v}\right)^2$$

we get:

$$MRT = \frac{a}{b}\,\frac{\frac{1}{a}\frac{da}{dx}}{\frac{1}{b}\frac{db}{dx}}\left\{1 - \frac{\frac{1}{2a}\frac{da}{dx}}{\frac{1}{b}\frac{db}{dx}}\right\}^2 \quad \ldots\ldots \quad (7)$$

For values of x for which $\frac{da}{dx} = 0$ and $\frac{2}{b}\frac{db}{dx} = \frac{1}{a}\frac{da}{dx}$ or $\frac{d\,log\frac{a}{b^2}}{dx} = 0$, the value of $T = 0$. Thus the same value of T always belongs to a couple of values of x which approach each other. And at the maximum value of T the two values of x have coincided. By differentiating (7) we get an equation which may be written in the form:

$$\frac{2a}{b}\frac{db}{dx} = \frac{3a\frac{d^2a}{dx^2} - 2\left(\frac{da}{dx}\right)^2}{a\frac{d^2a}{dx^2} - \left(\frac{da}{dx}\right)^2}\frac{da}{dx}$$

from which, taking (6) into consideration, we obtain again (4).

It appears from the foregoing that putting $a_{12}{}^2 = a_1\,a_2$ comes to the same thing as putting $m = 2$. For mixtures with minimum plaitpoint the value of m differs much from this value, as it is then smaller than 1, and so $a_{12}{}^2$ will have to differ pretty much from a_1a_2. If we put $a_{12}{}^2 = l^2\,a_1\,a_2$, in which $l^2 < 1$, we find from:

$$2\,a\frac{d^2a}{dx^2} = \left(\frac{da}{dx}\right)^2 + 4\,(1-l^2)\,a_1\,a_2$$

$$(2-m)\,a\frac{d^2a}{dx^2} = 4\,(1-l^2)\,a_1\,a_2$$

or

$$\left(1 - \frac{m}{2}\right)(a_1 + a_2 - 2a_{12})\,a = (1 - l^2)\,a_1\,a_2$$

It may be derived from this equation that m may lie near 2, even when l differs comparatively much from 1.

The value of a varying with x, also the ratio of $1 - \frac{m}{2}$ and $1 - l^2$ will vary with x. If we make a increase with x, which probably will be in general the case, then a_1 is the smallest value of a and

a_2 the greatest value, whereas the value of a for $x=\frac{1}{2}$ will be equal to $\frac{a_1+a_2+2a_{12}}{4}$.

So the ratio $\frac{1-\frac{m}{2}}{1-l^2}$ is for $x=0$, $x=\frac{1}{2}$ and $x=1$:

$$\frac{1-\frac{m}{2}}{1-l^2}=\frac{a_2}{a_1+a_2-2a_{12}}=\frac{\frac{a_2}{a_1}}{\left(\sqrt{\frac{a_2}{a_1}}-1\right)^2+2\,(1-l)\sqrt{\frac{a_2}{a_1}}}$$

$$\frac{1-\frac{m}{2}}{1-l^2}=\frac{4a_1\,a_2}{(a_1+a_2)^2-4a^2_{12}}=\frac{4\,\frac{a_2}{a_1}}{\left(\frac{a_2}{a_1}-1\right)^2+4\,(1-l^2)\,\frac{a_2}{a_1}}$$

$$\frac{1-\frac{m}{2}}{1-l^2}=\frac{a_1}{a_1+a_2-2a_{12}}=\frac{1}{\left(\sqrt{\frac{a_2}{a_1}}-1\right)^2+2\,(1-l)\sqrt{\frac{a_2}{a_1}}}$$

If we choose the second of these equations, from which it is easiest to draw conclusions with regard to the value of m at given value of l^2, we write it first in the following form:

$$\frac{2}{m}-1=\frac{4\,(1-l^2)\,\frac{a_2}{a_1}}{\left(\frac{a_2}{a_1}-1\right)^2}.$$

If we always take the same value of $1-l^2$, but different values of $\frac{a_2}{a_1}$, we find very great differences in the value of m. For instance with $\frac{a_2}{a_1}=2$ we have $\frac{2}{m}-1=8\,(1-l^2)$, or $m=\frac{2}{1+8\,(1-l^2)}$; but with $\frac{a_2}{a_1}=11$, m is found equal to $m=\frac{2}{1+0{,}44\,(1-l^2)}$. With $l^2=1$ we find of course in both cases $m=2$. But for smaller values of l the values of m differ considerably. For $l=0$ these values are $\frac{2}{9}$ and $\frac{2}{1{,}44}$.

If we had discussed the third of the equations, the values of m would have been found still higher. According to the first of the equations of course smaller.

Let us finally examine the course of the line $\left(\frac{dp}{dx}\right)_v = 0$ in the cases that there can be no contact with the line $\left(\frac{dp}{dv}\right)_x$, or only on the side of the liquid volumes. We saw already above, that then the locus of the points of intersection of the two curves mentioned (cf. 7) runs to greater volumes, if x is made to increase. Then at given T, only that part of the line $\left(\frac{dp}{dx}\right)_v = 0$ exists, for which this line runs to greater volume. The lefthand part, for which this curve may reach infinitely large volume lies in the common case at a value of x to be calculated from $MRT\frac{db}{dx} = \frac{da}{dx}$. Then $\frac{v-b}{v} = \sqrt{\frac{MRT\frac{db}{dx}}{\frac{da}{dx}}}$ and the first part of this equation is then equal to the unity, because $\frac{v}{b} = \infty$. But $\frac{v-b}{v}$ can also be equal to 1 in another case, viz.: if b should be $= 0$. This can only occur, when extrapolating we also admit negative values of x, and moreover choose for b such a function of x that it can become equal to 0 for negative value of x. This is the case for a linear function, but putting $b = b_1(1-x) + b_2x$ is only an approximation. Whether this can also be the case with a more exact shape of $b = f(x)$, must be left undecided. Moreover it is necessary, if we choose always greater negative value of x, that we first find $b = 0$, before finding $\frac{da}{dx} = 0$. But then the shape of the p-lines must also be modified. I shall however not enter into a discussion of this, for one reason because Dr. Kohnstamm informed me, that he had already been engaged in the study of the modified course of the isobars, and that he had also come to the conclusion that the relative situation of the values of x, for which $b = 0$ and $\frac{da}{dx} = 0$, is decisive. Moreover I leave undecided for the present whether also on other suppositions than $0 < x < 1$ there can be question of minimum plaitpoint temperature, which is to be distinguished from minimum value of $\frac{a_x}{b_x}$.

Botany. — "*Contribution* N°. 1 *to the knowledge of the Flora of Java.*" (Fourth continuation).[1]) By Dr. S. H. KOORDERS.

§ 7. Plantae Junghuhnianae ineditae. I. Notes on some javanese species of an as yet unpublished collection of Junghuhn's plants, in 's Rijks Herbarium at Leiden.

A few months ago, while searching in 's Rijks Herbarium at Leiden for some herbariumspecimens of JUNGHUHN's Javanese alpine plants, which were required by me, one of the officials of that institution found among the separately preserved collections of "*Indeterminata*" a fairly extensive collection made by JUNGHUHN. This collection had already undergone preliminary determination by me, in 1896 (during a short stay at Leiden), at the request of Dr. J. VALCKENIER SURINGAR, but for the rest remained wholly undetermined.

As I noticed in this collection a number of Javanese alpine plants, and as it seemed worth while to study the collection as a whole, I resolved to complete the determination, begun in 1896, and to publish the results. The latter, as far as an enumeration of the Javanese specimens is concerned, are ready for the press, but will be published separately; here I only append a few remarks on this collection of Junghuhn.

The whole collection consisted of fifteen large packets and fully 560 collecting numbers.

As is the case of very many old herbariumcollections, the labelling of a large number of these specimens left much to be desired. On the other hand some specimens were provided with detailed collecting labels, written by JUNGHUHN himself. With a few exceptions, all the specimens were quite undetermined (without determination of the genus and order). Most of the specimens were also without a collecting number on the label. In consultation with Dr. J. C. GOETHART, Keeper of 's Rijks Herbarium, it was accordingly decided to give running numbers to this whole collection of "*Plantae Junghuhnianae ineditae*", these numbers being independent of the old numbers, extant in some cases, but not explained by any list or publication. Printed labels have also been added, running partly as follows: "*Plantae Junghuhnianae ineditae. In insula Java legit* Dr. FR. JUNGHUHN *anno* 1838—1863 *sub n....*" Except for the substitution of the word "Sumatra" for "Java", the specimens from Sumatra in this collection have received a similar label.

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[1]) Continued from these Proceedings p. 132.

I have not been able to ascertain, why this extensive collection of JUNGHUHN's plants has not been worked at during so many decades, and apparently was never in the hands of MIQUEL. I surmise, in the first place, that it was not received from JUNGHUHN either until the period 1855—1864, or until after his death, *i.e.* after 1864; the receipt of the collection is noted on the outside in an unknown handwriting as "from Bandong". In the second place I surmise that this unpublished collection was accidentally mislaid among the mass of material in 's Rijks Herbarium at Leiden, and was consequently not found again, when MIQUEL was Director of that Institution (1862—1871).

For had this collection been in the hands of one, with so good a knowledge of the East Indian flora as that possessed by MIQUEL, there can, in my opinion, be no doubt, that he would at once have discovered the 9 species mentioned below, which at the time were new to the flora of Java and were found by me undetermined in 1896. Nor would these 9 species have been omitted from the Javanese flora in the publication [1]) "*Plantae Junghuhnianae*" of 1854 or in the other publications of MIQUEL (e. g. Flora Ind. Bat., Ann. Mus. bot. Lugd. Bat., etc.).

As such I mention the following species:

Pl. Jungh. inedit. n. 368, 380, 381, 385 and 394 = *Turpinia parva* KOORD. et VALETON (first published in 1903) Pl. Jungh. ined. n. 545 = *Ilex Hookeri* KING (has not yet been mentioned in the literature as occurring in Java), *Itea macrophylla* Wall. var. *minor* K. et V. (at the time not recorded in Java); Pl. Jungh. ined. n. 207 = *Aglaia heptandra* KOORD. et VALETON (first published in 1896);

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[1]) The title of this publication is: *Plantae Junghuhnianae. Enumeratio plantarum quas in insulis Java et Sumatra detexit* FR. JUNGHUHN, *Leiden*, 1854. In the Index Kewensis it is often quoted as MIQUEL Pl. Jungh., although MIQUEL's name does not appear in the title. Most of the phanerogams in this publication were treated of by MIQUEL himself, some other families by others *i.a.* by BENTHAM (*Leguminosae)*, MOLKENBOER (*Loranthaceae)*, W. H. DE VRIESE (*Primulaceae, Dipterocarpaceae*, etc.), HASSKARL (*Commelynaceae, Amaranthaceae)*, BÜSE (*Graminae)*, BURGERSDIJK (*Violaceae*), and A. J. DE BRUYN (*Polygonaceae*).

In the catalogue of the University library at Leiden, this publication *Plantae Jungh. Enumeratio plant. etc.* (1854) is stated to have appeared in 1851—1855.

In the only copy in 's Rijks Herbarium I found the year 1854 given as the date of publication. This bound copy ends with p. 552, where as the copy of the Royal Academy of Sciences at Amsterdam is slightly more complete, ending with p. 570. The publication seems to have been stopped prematurely, the less incomplete copy of the Royal Academy of Sciences ends on p. 570 *in the middle of a word* and is therefore evidently no more rounded off than the copy I found at Leiden. The date of publication is given on the title page of the latter copy as 1853.

Pl. Jungh. ined. n. 91 et 103 = *Mallotus campanulatus* J. J. Smith (first published in 1907 in Icones Bogoriensis); Pl. Jungh. ined. n. 113 = *Ostodes macrophylla* Benth. et Hook (not recorded for Java even at the present time); Pl. Jungh. ined. n. 462 = *Elaeocarpus Griffithii* A. Gray (not known for Java at that time); Pl. Jghn. ined. n. 438 = *Saurauja dasyantha* De Vriese (even now not mentioned for Java in the literature); Pl. Jghn. ined. n. 256 = *Eugenia cuprea* Koord. et Valeton published in 1900); Pl. Jghn. ined. n. 426 = *Symplocos Junghuhnii* (published for the first time below).

The specific description is as follows:

Symplocos Junghuhnii Koord., nova spec. — Arbor ramulis glabris. Folia tenuiter coriacea, supra glaberrima, subtus praeter costam laxe appresse pilosam glabra; 12—15 cm. longa et 4—5 cm. lata, subintegra v. valde indistincte serrulata, basi angustata, apice sensim vel abrupte acute acuminata; nervis secundariis plerumque impressis, petiolo 1—1$^{1}/_{2}$ cm. longo. Racemi simplices axillares et terminales villosi petiolo 4—5-plo longiores; bracteae ovato-acutae extus basi puberulae calycem aequantes; pedicelli calyce paullo breviores, calycis tubus extus villosus, lobi rotundati glabri marginibus ciliatis, corolla calyce duplo longior utrinque glabra stamina ultra 100 satis distincte pentadelpha; filamenta filiformia glaberrima; ovarium 3-loculare glabrum, stylus glaber; fructus ignotus.

West-Java (Preanger). — Pl. Jungh. ined. n. 426 in Herb. L. B.

The foliage of this species greatly resembles that of *Sympl. Henschelii* Brand [in Engler Monogr. Symploc. Pflanzenw. IV. 242. (1901) 89], but the floral structure is different, as is evident from the above diagnosis.

In the system of the Symplocacae of Brand l.c. this species will have to be placed in the subgenus *Hopea* (L. f.) Clarke, and in the section *Bobua* (DC.) Brand., and probably in the subsection *Palura* (Buch.-Hamilt.) Bent, et Hook., immediately near to *Symplocos ribes* Jungh. et De Vriese [in De Vriese, Pl. nov. Ind. bat. (1845) 11; Brand l.c. 39.] Through the extra-ordinarily large number (100) of stamens *Symplocos Junghuhnii* seems to me to differ from *S. ribes*, and from the other more or less closely related Javanese species, *S. aluminosa* Blume Brand l.c., *S. odoratissima* (Bl.) Choisy and *S. sessilifolia* (Bl.) Görke.

S. polyandra, Brand. l. c. 36 of the Philippines, which is also related and also has about 100 stamens, is distinguished from the Javanese plant since it has panicles instead of simple racemes.

In 1856 MIQUEL evidently resolved to bring out a second part of the publication, which appeared in 1854 (*Plantae Jungh. Enum. pl.*). This follows for instance from his quoting in the Flora Ind. Bat. II (1856) p. 1053: "Pl. Jungh. I. p. 84". My publication on the Pl. Jungh. ined. might therefore perhaps have been called "Pl. Jungh. II". Since, however the only part, which appeared in 1854, was not specially designated as part N°. I, I have now, for the sake of clearness, not called my present publication also "*Plantae Jungh.*", but "*Plantae Junghuhnianae ineditae*".

I found this latter designation for the first time in MIQUEL Fl. Ind. Bat. I. 2. (1859) p. 356. An authentic herbariumspecimen of *Flueggea serrata* MIQ., collected by JUNGHUHN in the higher mountain regions of Java, and found by me in the University Herbarium at Utrecht, is published there for the first time and is quoted by MIQUEL l. c. as *Pl. Jungh. inedit.*

The authentic herbarium-labels, preserved at Leiden, which refer to the species treated of in the above-mentioned publication (*Pl. Jungh. Enum. pl.*, 1854) bear numbers, which correspond with that publication of 1854 and are sometimes also quoted in the later publications as *Pl. Jungh. n.* 1, 2, 3, etc. In order to avoid any possible confusion with these numbers, I have quoted below the specimens in the collection now described by me, as follows: *Pl. Jungh. ined. n.* 1, 2, etc.

The number of exclusively alpine Javanese species met with in the above collection, is not large. Nevertheless I found several more or less characteristic Javanese alpine species represented, sometimes by a profusion of specimens. As such the following may be mentioned among others: *Urtica grandidenta* MIQ., *Thalictrum javanicum* BL., *Myrica javanica* BL., *Euphorbia Rothiana* SPRENG., *Viola serpens* WALL., *Leptospermum javanicum* BL., *Clethra canescens* REINW., *Leucopogon javanicus* (JUNGH.) DE VRIESE, *Lysimachia ramosa* WALL. var. *typica* KNUTH., *Primula imperialis* JUNGH., *Buddleia asiatica* LOUR., *Vaccinium Teijsmanni* MIQ., *Vaccinium varingaefolium* MIQ., *Rhododendron retusum* BENN., *Lonicera oxylepis* MIQ., etc.

With some specimens of the collection, now described by me, I found labels, on which, presumably about half a century ago, was written in the hand-writing of the late Professor W. H. DE VRIESE: "*legit Junghuhn, herb. de Vriese*". It seems therefore, that before 's Rijks Herbarium at Leiden acquired this collection of Junghuhn whether by purchase or by donation, it belonged wholly or partly to that herbarium.

The determination of the above-mentioned JUNGHUHN's collection, was chiefly carried out by me at Leiden, with the aid of the material for comparison in 's Rijks Herbarium, and for a few rare species with the help of the collections of the University Herbarium at Utrecht.

Leiden, Juni 23rd 1908.

Chemistry. — "*The dynamic conception of a reversible chemical reaction.*" By Prof. A. Smits and J. P. Wibaut. (Communicated by Prof. A. F. Holleman.)

It is generally known that our kinetic views lead to the assumption, that with every reversible reaction we meet with two reactions, which proceed in opposite directions.

The following consideration, however, seemed to show that a direct proof for this dynamic conception could not be given.

Our power of observation only enables us to observe differences; so if we observe something of a conversion, this is the consequence of this that the velocity of one reaction is greater than that of another, and we get an impression as if only one reaction takes place, which proceeds with a velocity equal to the difference of the velocities of the two reactions.

As we shall see, this reasoning, which is perfectly correct for conversions in *homogeneous* systems, does, however, not hold good in all respects in a single case for a conversion in a *heterogeneous* system in consequence of particular circumstances.

The above arguments, however, seemed so convincing that up to now the following *indirect* proof has been considered the only one possible.

The already indicated conception of a reversible reaction leads to a simple relation between the constants of equilibrium and the two constants of reaction, which runs: $K = \frac{k_1}{k_2}$. This relation, now, supplied a means to test the kinetic conception of a reversible conversion, and it is known that experiment has shown for the few cases which have as yet been investigated, that this relation is really satisfied.

Yet it seemed very desirable to prove the correctness of our dynamic conception of a reversible reaction by a *direct* way.

The conversion by means of which we have reached our purpose is this

$$2\,CO \rightleftarrows CO_2 + C.$$

That the choice fell on this reaction was due to this that it has appeared from the investigations of BOUDOUARD[1]) and others that when CO is converted into CO_2 and C, the carbon is deposited in the form of graphite, so that it was to be expected that when we start from the righthand system, and lead CO_2 over *diamond* at constantly increasing temperature, graphite, which will be immediately visible even in exceedingly small quantities will deposit on the diamond, the reaction proceeding simultaneously from left to right.

[It is hardly necessary to observe here that we discuss the reaction in the gas phase, in which the gaseous carbon is one of the reading components.

The circumstance that the system is heterogeneous, and according to the molecular theoretical views by the side of the homogeneous reaction two more heterogeneous transformations take place, viz.: diamond → C_{vapour} and C_{vapour} → graphite, between which the homogeneous reaction forms the link, made us suppose, we had found in this example a means to test our dynamic conception concerning a chemical reaction][2]).

It is self-evident that if the experiment is to prove anything, care must be taken that the temperature never falls, because in this case the depositing of graphite might be ascribed to a shifting of the equilibrium from left to right.

To be sure that this was out of the question it was desirable to make the temperature constantly increase during the experiment.

Before proceeding to the experiment we gladly avail ourselves of this opportunity to mention that the diamond powder with which the above mentioned investigation was made, had been kindly supplied to us by Messrs. ASSCHER, to whom we here express our great indebtedness.

As it was important for our investigation to start from white diamond powder, the diamond received by us, which had a grey colour in consequence of impurities, was heated in an open china mug, by means of which a perfectly white powder was obtained.

Before now proceeding to the decisive experiment, it was necessary to investigate first of all whether at the temperature at which we intended to perform our investigation, diamond is already converted to graphite.

For this purpose the white diamond powder was heated for an hour to 900° in an atmosphere of pure nitrogen by means of an electrical furnace, on which it appeared that under these circumstances nothing was to be detected of a conversion of diamond into graphite.

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[1]) Ann. Chim. Phys. (7) **24**, 5—85 (1901).

[2]) The passage between [ ] is added in the English translation.

When this favourable result had been obtained, a china dish filled with diamond powder was placed in a china tube which was slowly heated in an electrical furnace, a current of pure CO_2 passing through the china tube.

The escaping gas was led through a very sensitive solution of $PdCl_2$, so that the presence of CO in it was at once to be detected.

The experiment showed that under these circumstances the reduction of CO_2 by diamond begins to be noticeable only at about 750°, and proceeds rapidly at 850°.

So after the conversion

$$CO_2 + C \rightarrow 2CO$$

had been shown in this way, we had to ascertain whether the reverse reaction

$$2CO \rightarrow CO_2 + C$$

had taken place in the course of this process.

For this purpose the CO_2 stream was suddenly broken while the temperature was still increasing, and the gas-mixture in the china tube was expelled rapidly and completely by means of pure nitrogen. Only then the temperature was lowered, and the furnace cooled down to the temperature of the room.

The contents of the boat showed in an unmistakable way that the latter reaction had really taken place, for the colour had become grayish, in consequence of the depositing of graphite, which had taken place throughout the mass.

On repetition of the experiment the same result was obtained, so that we think that we have given in this way for the first time a *direct* proof of the correctness of the *dynamic* conception of a reversible reaction.

Amsterdam, June 1908.

Anorg. chem. Laboratorium
of the University.

Physics. — "*The P-T-X-spacial figure for a system of two components which are miscible in the solid or liquid crystalline state in all proportions.*" By Prof. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS).

When we project the spacial figure mentioned in the title above it appears that its most remarkable feature is this that three two sheet surfaces must intersect viz. the vapour-liquid sheet, the vapour-mixed-crystal sheet, and the liquid-mixed-crystal sheet, of which we know that for the simplest case, i.e. for the case that these sheets possess neither maximum nor minimum, they show great resemblance in form.

To examine how this intersection takes place we consider first of all a p-x-figure for a temperature below the triplepoint temperature of the two components.

If we call as is usual, the component with the highest vapour tension (and the lowest triple-point temperature) A, this p-x-diagram has a shape as indicated in fig. 1.

On line $a\,c\,b$ we find the mixed-crystal phases, which coexist with the vapour phases, which lie on the line $a\,d\,b$.

Between these two curves lies the region for vapour + mixed-crystal, $G + F$, and above the line $a\,c\,b$ the region for the mixed-crystals F, and under $a\,d\,b$ the region of the vapour G. If now we choose a temperature above the triple-point temperature of A, but below that of B, and if we assume for a moment that at the temperature considered A is found in a solid, so supersolidified state, we get a p-x-figure as indicated by $a\,f\,b\,g\,a$ in fig. 2, which is quite analogous to that represented in fig. 1.

Solid A, however, being metastable at this temperature, part of this p-x-figure will be metastable on the A-side, and now the question rises what stable equilibria will take the place of these metastable equilibria.

This is immediately seen when we imagine the case, that the two components are liquid at the temperature considered, and so B occurs in superliquefied state.

In this case we should find a p-x-figure as indicated by $c\,l\,d\,g\,c$, where we notice that d lies below b, and c above a, b and c denoting the vapour tension of metastable states of A and B.

The line cld indicates here the liquid phases coexisting with vapour phases on cgg.

The p-x-figure $a\,f\,b\,g\,a$ being metastable on the side of A and $c\,l\,d\,g\,c$ being metastable on the side of B, it is at once evident tha the stable p-x-figure will contain the lefthand part of the former and the righthand part of the latter p-x-figure, which parts will meet where a vapour phase coexists at the same time with a liquid phase and with a mixed-crystal phase.

As follows from the diagram the vapour branches of the two p-x-figures intersect in g, so that g is a vapour which does not only coexist with the liquid l, but also with the mixed-crystal phase f. So the three-phase-equilibrium $G + L + F$, which is non-variant at constant temperature constitutes the transition between the series of mixed-crystal phases af, and the series of liquid phases ld, which can coexist at a series of pressures with vapour phases of different concentration.

We find the region of the liquid L above the line dl and the region of the mixed crystals F above the line af. The two regions are separated by a region of liquid + mixed crystals lying between the lines lq and fq.

If we now draw some p-x-figures corresponding with different temperatures in the same graphical representation beginning with the triple point temperature of A, and ending with the triple-point temperature of B, we get what is represented in fig. 3.

Figure ab corresponds to the triple point temperature of A and a_3b_3 to that of B, the p-x-figures a_1b_1 and a_2b_2 referring to intermediate temperatures.

From this collection of p-x-figures we see that when we join the corresponding points of the different three-phase-pressure lines glf, a three-phase-region is formed composed of two two-phase-regions, first of the two-phase-region for the equilibria between vapour and liquid, and secondly of a two-phase-region for the coexistence of liquid and mixed crystals.

If we think the p-x-diagrams corresponding with the different temperatures placed in succession, the vapour-lines form a vapour-sheet, the liquid-lines a liquid-sheet, and the mixed-crystal-lines a mixed-crystal-sheet.

The line bgg_1a_3 indicates the intersection of the vapour-sheet of the mixed-crystals[1]) with the vapour-sheet of the liquid phases, the line bll_1a_3 that of the liquid sheet of the mixed-crystals with the liquid sheet of the vapour phases, and bff_1a_3 the line along which the mixed-crystal sheet of the liquid phases intersects the mixed-crystal sheet of the vapour phases.

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[1]) By the vapour sheet of the mixed crystals we must understand here the vapour sheet coexisting with the mixed-crystal sheet.

All this becomes perfectly clear when we consider the spacial representation, fig. 4, to the *right* of the plane $v_1 v_2 v_3 v_4$.

S_A is the triplepoint of the component A

S_B „ „ „ „ „ „ B

cS_A is the vapour-pressure-line of solid A

$S_A K_A$ „ „ „ „ liquid A terminating in the critical point K_A.

aS_B is the vapour-pressure-line of solid B and

$S_B K_B$ „ „ „ „ liquid B terminating in the critical point K_B.

$S_A S'_A$ is the melting-point-line of A and $S_B S'_B$ the melting-point-line of B.

$S_A\, g\, S_B\, f\, S_A$ is the three-phase-region discussed before, and the v,x-section drawn between the triple-points S_A and S_B shows that $S_A\, g\, S_B$ is the vapour line, $S_A\, l\, S_B$ the liquid line, and $S_A\, f\, S_B$ the mixed-crystal line.

On the two-phase-region $S_A\, g\, S_B\, l\, S_A$ lie the vapour and liquid phases which are in equilibrium with the mixed-crystals, and on the two-phase-region $S_A\, l\, S_B\, f\, S_A$ are found the liquid and the mixed-crystal phases which can coexist with the vapour.

The two-sheet surface for mixed-crystal and liquid rests on this latter two-phase-region, which surface will in general be very steep. It has been assumed in the spacial figure that as is actually the case as a rule, $\frac{dp}{dt}$ of the melting-point lines of the components is at first positive, which causes the two-sheet surface mentioned to run to higher temperatures with increasing pressure, which is here represented in an exaggerated manner.

A consequence of this situation is this that, as has been indicated in the section, at a temperature lying between the triple-point temperatures of A and B, the region for liquid and mixed crystal ceases to exist above a certain pressure, r, so that the three regions of two-phase equilibria, mixed-crystal-vapour, liquid-vapour, and mixed-crystal-liquid are limited on all sides.

It is evident that when $\frac{dp}{dt}$ is negative for both melting-point lines, point r will not lie on the melting-point line of the component A, but on that of B.

In the case that the two components pass into the fluid-crystalline state before melting, the spacial figure of such a system is represented by the whole of figure 4 for the simplest case.

The lefthand part agrees then perfectly with BAKHUIS ROOZEBOOM's spacial figure, O_A and O_B not representing the melting-points under vapour-pressure, but the transition points of the two components under vapour pressure, i. e. the points where the ordinary crystalline state passes to the fluid crystalline state under the pressure of its vapour.

If this spacial figure is cut by a plane of constant pressure, we get, at least if this pressure is chosen high enough, the simplest imaginable T-X-figure of a system of two components, each of which possesses a stable fluid-crystalline modification.

The other possible cases may be easily derived from this spacial figure.

Amsterdam June 1908. *Anorg. Chem. Laboratorium*
of the University.

Physics. — "*The liquefaction of helium*". By Prof. H. KAMERLINGH ONNES. Communication N°. 108 from the Physical Laboratory at Leiden.

§ 1. *Method.* As a first step on the road towards the liquefaction of helium the theory of VAN DER WAALS indicated the determination of its isotherms, particularly for the temperatures which are to be attained by means of liquid hydrogen. From the isotherms the critical quantities may be calculated, as VAN DER WAALS did in his Dissertation among others for the permanent gases of FARADAY, which had not yet been made liquid then, either by first determining a and b, or by applying the law of the corresponding states. Led by the considerations of Comm. N°. 23 (Jan. 1896)[1]) and by the aid of the critical quantities the conditions for the liquefaction of the examined gas may be found by starting from another gas with the same number of atoms in the molecule, which has been made liquid in a certain apparatus. By a corresponding process in an apparatus of the same form and of corresponding dimensions the examined gas may be made liquid.

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[1]) [Developed in view of the statical liquefaction of hydrogen and the obtaining of a permanent bath of liquid hydrogen (Comm. N°. 94*f*) at which I was working then].

By [] will be designed additions made in the translation.

The **Joule-Kelvin** effect, which plays such an important part in the liquefaction of gases whose critical temperature lies below the lowest temperature down to which we can permanently cool down, may be calculated from the isotherms, at least if the specific heat in the gas state is not unknown, and its determination, though more lengthy than that of the isotherms, may be an important test of our measurements. If there is to be question of statical liquefaction of the gas by means of the **Joule-Kelvin** effect, this must at all events give a decrease of temperature at the lowest temperature already reached, which, as was demonstrated in the above communication, will be the case to a corresponding amount for gases with the same number of atoms [1] in the molecule at corresponding states, while a mon-atomic gas compared with a di-atomic one will be in more favourable circumstances for liquefaction (Comp. also Comm. N°. 66, 1900).

But the sign of the **Joule-Kelvin** effect under certain circumstances does not decide the question whether an experiment on the statical liquefaction of a gas will succeed. Speaking *theoretically*, when by the **Joule-Kelvin** effect, at a certain temperature a decrease of temperature however slight can be effected, liquid may be obtained by an adiabatic process with a regenerator coil and expansion cock with preliminary cooling down of the gas to that temperature. But as long as we remain too near the point of inversion the **Joule-Kelvin** effect will have a slight value; accordingly the processes by which really gas was liquefied in statical state with an apparatus of this kind, as those which were applied to air by **Linde** and **Hampson**, and to hydrogen by **Dewar**, start from a much lower reduced temperature, viz. from about half the reduced temperature at which the sign of the **Joule-Kelvin** effect at small densities is reversed, or more accurately from somewhat below the **Boyle**-point, i.e. that temperature at which the minimum of pv is found at very small densities. [Experiments from which could be derived at how much higher reduced temperature the process still succeeds with mon-atomic gases are lacking]. So according to the above theorem it is *practically* the question whether the lowest temperature at our disposal lies below this **Boyle**-point [2] which is to be calculated from the isotherms, and the **Joule-Kelvin** effect has therefore a sufficient value to yield an appreciable quantity of liquid in a given apparatus in a definite time.

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[1] [The inversion points of the effect having reference to the amount 0 and therefore being independent of the number of atoms in the molecule, are at corresponding states, and the inversion point for small densities is at corresponding temperature for *all* gases as far as they obey the law of corresponding states. This is easily deduced from the considerations of Comm. N°. 23].

[2] [The **Boyle** point, as well as the **Joule-Kelvin** inversion point for small densities is a corresponding temperature and both temperatures are therefore proportional theoretically. In the present question it is better to refer to the **Boyle** point than to the **Joule-Kelvin** inversion point considering the deviations of the law of corresponding states].

Three years ago I had so far advanced with the investigations which led to the isotherms of helium,1) that these determinations themselves could be taken up with a reasonable chance of success.

At first the great difficulty was how to obtain sufficient quantities of this gas. Fortunately the Office of Commercial Intelligence at Amsterdam under the direction of my brother, Mr. O. **Kamerlingh Onnes**, to whom I here express my thanks, succeeded in finding in the monazite sand the most suitable commercial article as material for the preparation, and in affording me an opportunity to procure large quantities on favourable terms. The monazite sand being inexpensive, the preparation of pure helium in large quantities became chiefly a matter of perseverance and care. 2)

The determination of isotherms of helium was not accomplished before 1907.

The results of the determinations of the isotherms were very surprising. They rendered it very probable that the **Joule-Kelvin** effect might not only give a decided cooling at the melting point of hydrogen, but that this would even be considerable enough to make a **Linde-Hampson** process succeed.

Before the determinations of the isotherms had been performed I had held a perfectly different opinion in consequence of the failure of **Olzewski**'s and **Dewar**'s attempts to make helium liquid, and had even seriously considered the possibility that the critical temperature of helium, might lie if not at the absolute zero-point, yet exceedingly low. In order to obtain also in this case the lower temperatures, which among others are necessary for continuing the determinations of isotherms below the temperatures obtainable with solid hydrogen, I had e.g. been engaged in designing a helium motor (cf. Comm. N°. 23) in which a vacuumglass was to move to and fro as a piston in another as a cylindre. And when compressed helium was observed to sink in liquid hydrogen (Comm. N°. 96, Nov. 1906) I have again easily suffered myself to be led astray to the erroneous supposition of a very low critical temperature.

In the meantime I had remained convinced that only the deter-

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1) [Comp. for cryostats: Comm. Ns. 14, 51, 83, 94, for thermometry: Comm. Ns 27, 60. 77, 93, 95, 99, 101, 102, for manometers, piezometers and determination of isotherms: Comm. Ns 44, 50, 69, 70, 71, 78, 97 99, 100].

2) [Even the quantity of 200 liters (and 160 liters of reserve) of the extreme purity required, though requiring a great deal of labour, was not out of reach].

mination of the isotherms could decide how helium could be made liquid. Hence we had proceeded with what might conduce to making a favourable result for the critical temperature at once serviceable. Thus the preparation of a regenerator coil with expansion cock in vacuum glass (to be used at all events below the point of inversion), and the preparation of pure helium was continued. Of the latter a quantity had even been gradually collected sufficiently large to render a determination of the JOULE-KELVIN effect in an apparatus already put to the test in prelimininary investigations possible, and to enable us to make efficient expansion experiments.

All at once all these preparations proved of the greatest importance when last year (Comm. N°. 102*a*) the isotherms began to indicate 5° K to 6° K for the critical temperature, an amount which according to later calculations, which will be treated in a subsequent paper, might have been put slightly higher (e. g. 0,5), and which was in harmony with the considerable increase of the absorption of helium by charcoal at hydrogen temperatures, on the strength of which DEWAR had estimated the critical temperature of helium at 8° K. For according to the above theorem it was no longer to be considered as impossible to make helium liquid by means of a regenerator coil, though this was at variance with the last experiments of OLSZEWSKI, who put the critical temperature below 2°.

It is true that the conclusions drawn from the isotherms left room for doubt. It seemed to me that the isotherms at the lowest temperature yielded a lower critical temperature than followed from the isotherms at the higher temperatures, which is due to peculiarities, which have been afterwards confirmed by the determination of new points on the isotherms. So there was ample room for fear that helium should deviate from the law of the corresponding states, and that still lower isotherms than those already determined should give a still lower critical temperature than 5° K., and according as the critical temperature passed on to lower temperatures the chance to make helium liquid by means of the JOULE-KELVIN effect beginning at the lowest temperatures to be reached with liquid hydrogen (solid hydrogen brings new complications with it) became less. This fear could not be removed by the expansion experiment which I made some months ago, and in which I had thought I perceived a slight liquid mist. (Comm. N°. 105 Postscriptum March 1908). For in the first place only an investigation made expressly for the purpose could decide whether the mist was distinct enough, and whether the traces of hydrogen the presence of which was still to be demonstrated spectroscopically, were slight enough to allow us to attach any importance to the phenomenon. And in the second place the mist was very faint indeed, which might point to a lower critical temperature than had been derived.

So it remained a very exciting question what the critical temperature of helium would be. And in every direction in which after the determination of the isotherms in hand we might try to get more information about it, we were confronted by great difficulties.

As, however, they consisted in the arrangement of a cycle with cooled helium, [this being indispensable to integrate cooling effects with a reasonable quantity of helium] the labour spent for years on the arrangement of the Leiden cascade of cycles for accurate measurements, might contribute to the surmounting of them. Arrived at this point I resolved to make the reaching of the end of the road at once my purpose, and to try and effect the statical liquefaction of helium with a circulation, as much as possible "corresponding" to my hydrogen circulation.

In this I perfectly realized the difficulty to satisfy at the same time the different conditions for success [allowing for possible deviations from the law of corresponding states]. For [though the suitability of the hydrogen cycle for the cooling down of the compressed helium to 15° K. was amply proved (Comm. N°. 103)] the preliminary cooling to be reached was, as to the temperature, only just within the limit at which it could be efficient, nor were the other circumstances which could be realized, any more favourable.

Of course the scale on which the apparatus intended for the experiment in imitation of the apparatus which had proved effective for hydrogen, would be built, was not only chosen smaller in agreement with the value of *b* which was put lower, but taken as small as possible. That the reduction of HAMPSON's coil to smaller dimensions does not diminish its action had been found by former experiments, and has been very clearly proved by what OLSZEWSKI tells about the efficiency of his small hydrogen apparatus. I could not, however, reduce below a certain limit without meeting with construction problems, about which the hydrogen apparatus had not given any information. We had to be sure that the capillaries would not get stopped up, that the cocks would work perfectly, that the conduction of heat, friction etc. would not become troublesome. When in connection with the available material, the smallest scale at which I thought the apparatus still sufficiently trustworthy, reduction to half its size, had been fixed, the dimensions of the regenerator coil, though as small as those of OLSZEWSKI's coil, proved still so large that the utmost was demanded of the dimensions of the necessary vacuum glasses; which was of the more importance, because the bursting of the vacuum glasses during the experiment would not only be a most unpleasant incident, but might at the same time annihilate the work of many months.

Besides the difficulties given by the helium liquefactor itself, the further arrangement of the cycle in which it was to be inserted, offered many more.

The gas was to be placed under high pressure by the compressor, and was to be circulated with great rapidity. Every contamination was to be avoided, and the spaces which were to be filled with gas under high pressure were to have such a small capacity, that they only held part of the available naturally restricted quantity of helium.

As compressor only CAILLETET's modified compressor could be used, a compressor with mercury piston, which had been arranged for experiments with pure and costly gases, and was described in Comm. N°. 14 (Dec. 1894) and Comm. N°. 54 (Jan. 1900), and which also served for the compression of the helium in the expansion experiments of last March (Comm. N°. 105)[1].

That it could only be charged to 100 atms., a fact which I had sometimes considered as a drawback in the case of experiments with helium, could no longer be deemed a drawback after the determinations of isotherms had taught that even if the pressure of helium compressed above 100 atms. at low temperatures is raised much, the density of the gas increases but little. Accordingly I had not gone beyond 100 atms. in my expansion experiments. The higher pressures which DEWAR and OLSZEWKSKI applied in their expansion experiments, have been a decided disadvantage, because they involved the use of a narrower expansion tube. With regard to the circulation now to be arranged, with estimation of the critical pressure at 7 or 5 atms.[2]), according as b was put at a third or half that of hydrogen, a pressure of 100 atms. in the regenerator coil had to be considered as sufficient according to the law of corresponding states.

But for a long time it was considered an insuperable difficulty that the compressor conjugated to the auxiliary compressor could circulate at the utmost 1400 liters of gas measured at the ordinary temperature per hour, $^1/_{15}$ of the displacement with the hydrogen circulation. Not before experiments with the latter had been made, in which the preliminary cooling of the hydrogen did not take place with air evaporating at the vacuumpump (so at — 205°) but under ordinary pressure (so at — 190°), and moreover the hydrogen compressor ran 4 times more slowly than usual, and in these experiments liquid hydrogen had yet been obtained, it might be assumed that the circulation process to be realized would still be sufficient to accumulate liquid helium.

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[1] [Just as when it was used to get a permanent bath of liquid oxygen (completed 1894 Comm. N⁰. 14) it was now again in the pioneering cycle and rewarded well the work spent on it, especially in 1888 when I was working at the problem to pour off liquid oxygen in a vessel under atmospheric pressure by the help of the ethylene cycle].

[2] [The results of the isotherm of helium at — 259° to be treated in a following communication were not yet available then; they point to a smaller value].

With regard to the parts of the compressors, the auxiliary apparatus, and the conduits, which in the course of the experiment assume the same pressure as the regenerator coil, their joint capacity was small enough to enable us to make the experiment with a quantity of 200 liters. This quantity of pure helium besides a certain quantity [160 liters] kept in reserve could be ready within not too long a time[1].

A great difficulty of an entirely different nature than the preceding one consisted in this that the hydrogen circulation and the helium circulation could not be worked simultaneously with the available helpers to work them. It is true that the two circulations have been arranged not only for continuous use, but if there is a sufficient number of helpers, also for simultaneous use, but in a first experiment it was out of the question to look, besides after the helium circulation, also after the hydrogen circulation, the working of which requires of course, great experience[2]. So on the same day that the helium experiment was to be made, a store of hydrogen had to be previously prepared large enough to provide for the required cooling during the course of the helium experiment. It was again the law of corresponding states which directed us in the estimation of the duration of the experiment and the required quantity of liquid hydrogen[3]. They remained just below the limit at which the arrangement of the experiment in the designed way would be unadvisable, but how near this limit was has appeared later.

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[1] [That success was only possible by applying the cycle method is evident from the fact that the helium has passed the valve 20 times before liquefaction was observed, and the considerable labour expended on the preparation of the pure helium would have been increased in the same proportion i.e. to an extravagant amount].

[2] [Now the great difficulties of a first liquefaction have been overcome simultaneous working has become possible, though it remains the question how to find the means to develop the laboratory service according to the extension of its field of research].

[3] [The hydrogen cycle is not only arranged so that the same pure hydrogen in it can be circulated and liquefied at the rate of 4 liters per hour as long as this is wished, but also allows (as will be treated in a following communication) easily to prepare great stores of extremely pure hydrogen gas, which can be tapped off from the apparatus as liquid at the rate of 4 liters per hour].

In all these considerations the question remained whether everything that could appear during the experiment, had been sufficiently taken into account in the preparation. So we were very glad when the calculation of the last determined points on the isotherm of — 259° shortly before the experiment confirmed that the BOYLE-*point* [though below the boiling point of hydrogen] lay somewhat above this lowest temperature of preliminary cooling, and at least the foundation of the experiment was correct.

In the execution I have availed myself of different means which DEWAR has taught us to use. I have set forth the great importance of his work in the region of low temperatures in general elsewhere (Comm. Suppl. N°. 9, Febr. 1904), here, however, I gladly avail myself of the opportunity of pointing out that his ingenious discoveries, the use of silvered vacuum glasses, the liquefaction of hydrogen, the absorption of gases in charcoal at low temperatures, together with the theory of VAN DER WAALS, have had an important share in the liquefaction of helium.

§ 2. *Description of the apparatus.* The whole of the arrangement has been represented on Pl. I. We mentioned before that in virtue of the principles set forth in Comm. N°. 23 the construction of the helium liquefactor (see Pl. II and III) was as much as possible an imitation of the model of the hydrogen liquefactor described before (Comm. N°. 94^f, May 1906), to which I therefore refer in the first place.

It was particularly difficult to keep the hydrogen, which evaporating under a pressure of 6 cm. is to cool the compressed helium to 15° K. (just above the melting point of hydrogen), on the right level in the refrigerator intended for this purpose. This difficulty was surmounted in the following way. The liquid hydrogen is not immediately conveyed from the store bottles into the refrigerator, but first into a graduated glass *Ga* in the way indicated before, which on comparison of the figures from Comm. N°. 94*f* and N°. 103 Pl. I fig. 4 does not require a further explanation. This graduated glass was a non-silvered vacuum glass, standing in a silvered vacuum glass *Gb* with liquid air, in which on either side the silver coating had been removed over a vertical strip so as to enable us to watch the level of the hydrogen in the graduated glass. From this vacuum glass the liquid hydrogen is siphoned over into the hydrogen refrigerator by means of a regulating cock *P*. To see whether the level of the liquid in the refrigerator takes up the right position, the german silver reservoir N_1 of a helium thermometer has been soldered to the tube which conveys at an initial temperature of — 190° the compressed helium which is to be cooled down further. This reservoir leads through a steel capillary N_2 (as in Comm. N°. 27, May, 1896) to a reservoir N_4 with stem N_3. The quantity of helium and the pressure have been regulated in such a way that the mercury stands in the top of the stem, when the thermometer reservoir is quite immerged in hydrogen of 15° K, while as soon as the level falls, this is immediately shown by the fall of the mercury. The same purpose is further served by two thermo-elements constantan iron (see Comm. N°. 89 Nov. 1903 and N°. 95*a* June 1906) one on the bottom, the other soldered to the spiral on the same level as the thermometer reservoir. They did not indicate the level in the experiment of July 10th, because something got defect.

The evaporated hydrogen contributes in the regenerator *Db* to save liquid air during the cooling of the compressed helium, and is sucked up (along 15 and *Hc*) in the large cylindre of the conjugated methylchloride pump (Comm. N°. 14 Dec. 1894), which otherwise serves in the methylchloride circulation of the cascade for liquid air; it is further conducted through an oil-trap, and over charcoal to the hydrogen gas-holder (Comm. N°. 94*f*), from which the hydrogen compressor (Comm, N°. 94*f*) forces the gas again into the store cylindres.

To fill the helium circulation the pure helium passes from the cylindres R_1 (see Pl. II), in which it is kept, into the gasholder floating on oil (cf. Comm. N°. 94*f*), which is in connection with the space in which the helium expands when issuing from the cock, a german silver cylindre, in which the upper part of the vacuum glass *Ea* has been inserted. The gas from the gasholder, and afterwards the cold outflowing helium, which has flowed round the regenerator coil, and of whose low temperature we have availed ourselves in the regenerator *Da* to save liquid air when cooling the compressed helium, is sucked up by the auxiliary compressor *V*, and then received in the compressor with mercury piston *Q* (Comp. Comm. N°. 54). This forces it (Pl. II and III) along the conduit:

a. through a tube *Ca* which at its lower end is cooled down far below the freezing point by means of vapour of liquid air, and at its upper end is kept at the ordinary temperature. Here the helium is perfectly dried.

b. through a tube divided into two parts along two refrigerating tubes (in *Da* and *Db*), in which it is cooled in the one by the abduced hydrogen, in the other by the abduced helium, after which it unites again.

c. through a tube *Cb* filled with exhausted charcoal immerged in liquid air. Here whatever traces of air might have been absorbed during the circulation, remain behind.

d. through a refrigerating tube B_3 lying in the liquid air, which keeps the cover of the hydrogen space and of the helium space cooled down.

e. through a refrigerating tube B_2, in which it is cooled by the evaporated liquid hydrogen.

f. through the refrigerating tube B_1 lying in the liquid hydrogen evaporating under a pressure of 6 cm., here the compressed helium is cooled down to 15° K;

g. and from here in the regenerator coil A, which has been fourfold wound as in HAMPSON's apparatus for air, and in the hydrogen liquefactor of Comm. 94*f*.

Then it expands through the cock M_1, if it should allow too much gas to pass, this can escape through a safety tube. When the temperature has descended so low that the liquid helium flows out, the latter collects in the lower part of the vacuum glass *Ea*, which is transparent up to the level of the cock, and is silvered above it.

The outflowing gaseous helium can be made to circulate again by the compressor of the circulation, or be pressed in the supply cylinders R_2.

At some distance under the expansion cock M_1, the german silver reservoir Th_1 of a helium thermometer has been adjusted, it is soldered to a steel capillary Th_2, which is connected with the manometer reservoir Th_4 with stem Th_3. If the mercury has been adjusted in such a way that at 15° K its level is at the lower end of the just mentioned stem, the stem has sufficient length to prevent the mercury from overflowing into the capillary with further fall of the temperature.

The circulation is provided with numerous arrangements for different operations (for the compressor comp. Comm. n°. 54). Worth mentioning is an auxiliary tube Z filled with exhausted charcoal, which is cooled by liquid air when used After the whole apparatus has been filled with pure gas, the gas is circulated through this side-conduit (along 11 and 8) while the tube *Cb* of charcoal belonging to the liquefactor, is shut off (by M and 9), to free it from the last traces of air which might have remained in the compressor and the conduits.

It now remains to describe in what way it has been arranged that the liquid helium can be observed. Round the transparent bottom part of the vacuum glass a protection of liquid hydrogen has been applied. The second vacuum glass E_b, which serves this purpose, forms a closed space together with the former E_a, and the construction has been arranged in such a way that first this space can be exhausted and filled with pure hydrogen gas, which is necessary to keep the liquid hydrogen perfectly clear later on. The liquid hydrogen is again conducted into this space in the way of Comm. N°. 94*f* and 103 Pl. I fig. 4; the evaporated hydrogen escapes at *Hg* to the hydrogen gasholder. The hydrogen glass is surrounded by a vacuum glass E_c with liquid air, which in its turn is surrounded by a glass E_d with alcohol, heated by circulation.

By these contrivances and the extreme purity of the helium we succeeded in keeping the apparatus perfectly transparent to the end of the experiment, after 5 hours. Protection with liquid hydrogen is necessary to reduce the evaporation of the helium to an insignificant degree notwithstanding that the silver coatings of the vacuum glass have been removed. That it ended in a narrower part, and the helium thermometer reservoir not was placed at the lowest point, was because it was possible that only an exceedingly slight amount of liquid was formed. The vacuum glass was made transparent up to the cock in order to enable us to see any mist that might appear and if on the other hand much liquid was formed, to prevent the lower part from getting entirely filled without our noticing it. The latter has actually been the case for some time, and would not have been so soon perceived, if the walls had been silvered further. But if the glass is not silvered, the conduction of heat towards the helium is much greater, and without protection with liquid hydrogen the helium that was formed, might have immediately evaporated.

In the preparation of the vacuumglasses [1]) Mr. O. KESSELRING, glassblower of the laboratory, has met the high demands put to him, with untired zeal and devotion, for which I here gladly express my thanks to him.

§ 3 *The helium.* As to the chemical part of the preparation of this gas I was successively assisted by Mr. J. WATERMAN, Mr. J. G. JURLING, Mr. W. MEYER-CLUWEN and Mr. H. FILIPPO Jzn. Chem. Docts., who collaborated with Mr. G. J. FLIM, chief of the technical department of the cryogenic laboratory. To all of them I gladly express my indebtedness for the share each of them has had in the arrangement, the improvement, and the simplification of the operation. More particularly to Mr. FILIPPO for his careful analyses and the effective way, in which the last combustion over CuO with addition of oxygen, and avoidance of renewed contamination by hydrogen was carried out by him.

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[1]) [There was one of each in reserve before the beginning of the experiment. Only one of the reserves had to be used].

The gas was obtained from the monazite (see § 1) by means of heating, it was exploded with oxygen, cooled with liquid air, and, compressed, led over charcoal at the temperature of liquid air. Then it was burned over CuO. Then it was compressed over charcoal at the temperature of liquid air, after which it was under pressure led over charcoal at the temperature of liquid hydrogen several times till the gas which had been absorbed in the charcoal and then separately collected no longer contained any appreciable admixtures.

This way of preparation (to be treated in a following Comm.) was also applied in Comm. N°. 105.

§ 4. *The experiment.* After on July 9th the available quantity of liquid air had been increased [1]) to 75 liters, all apparatus examined as to their closures, exhausted, and filled with pure gas, we began the preparation of liquid hydrogen on the 10th of July, 5.45 a.m., 20 liters of which was ready for use in silvered vacuum glasses (cf. Comm. N°. 94*f* Pl. III) at 1.30 p.m. In the meantime the helium apparatus had been exhausted while the tube with charcoal belonging to it was heated, and this tube being shut off, the gas contained in the rest of the helium circulation was freed from the last vestiges of air by conduction over charcoal in liquid air through the side-conduit. The hydrogen circulation of the helium apparatus was connected with the hydrogen gasholder and the air-pump, which had served as methyl chloride pump in the preparation of air the day before, and this whole circulation was exhausted for so far as this had not yet been done, and filled with pure hydrogen. Moreover the space between the vacuum glasses (E_a and E_b) which was to be filled with liquid hydrogen as a protection against access of heat, was exhausted and filled with pure hydrogen, and the thermometers and thermoelements were adjusted.

At 1.30 p.m. the cooling and filling of the glasses which, filled with liquid air, were to protect the glasses which were to be filled with liquid hydrogen, began with such precautions that everything remained clear when they were put in their places. At 2.30 a commencement was made with the cooling of the graduated vacuum glass and of the hydrogen refrigerator of the helium liquefactor by the aid of hydrogen led through a refrigerating tube, which was immerged in liquid air. At 3 o'clock the temperature of the refrigerator had fallen to — 180° according to one of the thermo-elements. Then the protecting glass (E_b) was filled with liquid hydrogen, and after some delay in consequence of insignificant disturbances, the filling of the graduated vacuum glass and the hydrogen refrigerator with hydrogen began at 4.20 p.m.

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[1]) [With the help of the regenerative cascade Comp. Comm. N°. 94, f. XIII and Supplem. N°. 18].

At the same time the helium was conducted in circulation through the liquefactor. The pressure under which the hydrogen evaporated, was gradually decreased to 6 c.m., at which it remained from 5.20 p.m. The level in the refrigerator was continually regulated according to the indication of the thermometer-level-indicator and the reading of the graduated glass, and care was taken to add liquid hydrogen (*Hydr. a*, *Hydr b* Pl. II) and liquid air wherever necessary (*a,b,c,d*, Pl. II). In the meantime the pressure of the helium in the coil was slowly increased, and gradually raised from 80 to 100 atms. between 5.35 and 6.35 p.m.

At first the fall of the helium thermometer which indicated the temperature under the expansion cock, was so insignificant, that we feared that it had got defect, which would have been a double disappointment because just before also in the gold-silver thermo-element, which served to indicate the same temperature, some irregularity had occurred. After a long time, however, the at first insignificant fall began to be appreciable, and then to accelerate. Not before at 6.35 an accelerated expansion was applied, on which the pressure in the coil decreased from 95 to 40 atms., the temperature of the thermometer fell below that of the hydrogen. In successive accelerated expansions, especially when the pressure was not too high, a distinct fluctuation of the temperature towards lower values was clearly observed Thus the thermometer indicated e.g. once roughly 6° K.

In the meantime the last bottle of the store of liquid hydrogen was connected with the apparatus: and still nothing had as yet been observed but some slight waving distortions of images near the cock. The thermometer indicated first even an increase of temperature with accelerated expansion from 100 atms., which was an indication for us to lower the circulation pressure to 75 atms. Nothing was observed in the helium space then either, but the thermometer began to be remarkably constant from this moment with an indication of less than 5° K. When once more accelerated expansion from 100 atms. was tried, the temperature first rose, and returned then to the same constant point.

It was, as prof. SCHREINEMAKERS, who was present at this part of the experiment, observed, as if the thermometer was placed in a liquid. This proved really to be the case. In the construction of the apparatus (see § 2) it had been foreseen that it might fill with liquid, without our observing the increase of the liquid. And the first time the appearance of the liquid had really escaped our observation. Perhaps the observation of the liquid surface, which is difficult for the first time under any circumstance, had become the more difficult as it had hidden at the thermometer reservoir. However this may be, later on we clearly saw the liquid level get hollow by the blowing of the gas from the valve and rise in consequence of influx of liquid on applying accelerated expansion, which even continued when the pressure descended to 8 atms. So there was no doubt left that the critical pressure lies also above one atmosphere. If it had been below it, the apparatus might all at once have been entirely filled with liquid compressed above the critical pressure, and only with decrease of pressure a meniscus would have appeared somewhere in the liquid layer; this has not taken place now.

The surface of the liquid was soon made clearly visible by reflection of light from below, and that unmistakably because it was clearly pierced by the two wires of the thermoelement.

This was at 7.30 p. m. When the surface had once been seen, it was no more lost sight of. It stood out sharply defined like the edge of a knife against the glass wall. Prof. KUENEN, who arrived at this moment, was at once struck with the fact that the liquid looked as if it was almost at its critical temperature. The peculiar appearance of the helium may really be best compared with that of a meniscus of carbonic acid e. g. in a Cagniard de la Tour-tube. Here, however, the tube was 5 cm. wide The three liquid levels in the vacuum glasses being visible at the same time, they could easily be compared; the difference of the hydrogen and the helium was very striking.

When the surface of the liquid had fallen so far that 60 cm³. of liquid helium still remained — so considerably more had been drawn off — the gas in the gasholder was exhausted, and then the gas which was formed from this quantity of liquid was again separately collected. In the course of the experiment the purity of this gas was determined by means of a determination of the density (2,01), which was afterwards confirmed by an explosion experiment with oxyhydrogen gas added, and further by a careful spectroscopical investigation.

At 8.30 the liquid was evaporated to about 10 cm³., after which we investigated whether the helium became solid when it evaporated under decreased pressure. This was not the case, not even when the pressure was decreased to 2,3 cm. A sufficient connection could not be quickly enough established with the large vacuumpump, which exhausts to 2 mm., so this will have to be investigated on another occasion. The deficient connection, however, has certainly made the pressure decrease below 1 cm., and perhaps even lower. That 7 mm. has been reached, is not unlikely.

At 9.40 only a few cm³. of liquid helium were left. Then the work was stopped. Not only had the apparatus been taxed to the uttermost during this experiment and its preparation, but the utmost had also been demanded from my assistants.

But for their perseverance and their ardent devotion every item of the program would never have been attended to with such perfect accuracy as was necessary to render this attack on helium successful.

In particular I wish to express my great indebtedness to Mr. G. J. Flim, who not only assisted me as chief of the technical department of the cryogenic laboratory in leading the operations, but has also superintended the construction of the apparatus according to my direction, and rendered me the most intelligent help in both respects.

§ 5. *Control experiments.* All the gas that had been used in the experiment, was collected in three separate quantities and compressed in cylindres. Quantity A contains what was finally left in the apparatus. Quantity B has been formed by evaporation of a certain quantity of liquid helium. Quantity C is the remaining part that has been in circulation. Together they yielded the same quantity as we started with. They were all three exploded with addition of oxyhydrogen gas and excess of oxygen ; no hydrogen could be demonstrated. For the density (in a single determination) we found $(0 = 16)$ $A = 2.04$, $B = 1.99$, $C = 2{,}02$).

The spectrum of the gas used for the experiment put in a tube with mercury closure without electrodes and freed beforehand from vapour of water and fat at the temperature of liquid air, answered (only the spectrum of the capillary has been investigated) the description given by Collie of the spectrum of helium with a trace of hydrogen and mercury vapour.

Spectroscopically both the distilled C, and B were somewhat purer than the original gas. In the latter the hydrogen lines gained in case of high vacua, in the former the helium disappeared last. The hydrogen, from which the latter has still been cleared, must be found in A. By means of absorption by charcoal 8 c.m³. of hydrogen was separated from this. To this would correspond a difference in percentage of hydrogen before and after the experiment of 0.004 °/₀.

To estimate the percentages of hydrogen the spectra of the just-mentioned quantities were compared with the spectrum of a helium which could not contain much more than 0.005 °/₀ hydrogen according to an estimation founded on the quantities of hydrogen which had been absorbed from the gas the last few times of successive purification when it was led compressed over charcoal at the temperature of liquid hydrogen, and with the spectrum of this helium after 0,1 °/₀ hydrogen had been mixed with it.

The gas used for the experiment did not differ much from that which served for comparison, and of which the red hydrogen and the helium lines vanished simultaneously for the highest vacua, but it seemed to be somewhat less pure, for the red hydrogen line preponderated over the helium line for the highest vacua. In the different spectra the hydrogen line was not to be seen at a pressure of 32 mm., the *F*-line with an intensity of 0,01 of He 5016; at 12—16 mm. *C* was faint compared with He 6677, and *F* faint compared with He 5016. An amount varying between 0,01 and 0,3 was assumed for the ratio of the intensity.

On the other hand at 32 mm. the *C* in the mixture with 0,1 pCt. hydrogen had already the same intensity as He 6677, *F* 0,3 of He 5016, which remained the case at 16 mm. (somewhat less for *C*, somewhat more for *F*).

In spite of the precautions taken it was observed a single time that the hydrogen lines increased in intensity during the determination, so when we proceeded to lower pressures the determinations became unreliable. These comparisons are, therefore, very imperfect; but then, the examination how traces of hydrogen in helium may be quantitatively determined by a spectroscopic method would constitute a separate investigation. In connection with the above difference in content of *B* and *C* with the original gas, the observations mentioned may perhaps serve to show that these percentages have not been much more than 0,004 and 0,008.

The purity of the helium had already been beyond doubt before, for the cock worked without the least disturbance, and no turbidity was observed even in the last remaining 2 cm³. of liquid.

The reliability of the helium thermometer was tested by the determination of the boiling point of oxygen, for which 89° K. was found instead of 90° K. We must however, bear in mind that the thermometer has not been arranged for this temperature and the accuracy in percents of the total value is considerably higher for the much lower temperature of liquid helium.

For the assistance rendered me in the different control experiments, I gladly express my thanks to Dr. W. H. Keesom and Mr. H. Filippo Jzn.

§ 6. *Properties of the helium.* By the side of important points of difference the properties of helium present striking points of resemblance with the image which Dewar drew in his presidential address in 1902 on the strength of different suppositions.

We mentioned already the exceedingly slight capillarity.

For the boiling-point we found 4°.3 on the helium thermometer of constant volume at 1 atm. pressure at about 20°K. This temperature is still to be corrected to the absolute scale by the aid of the equation of state of helium. The correction may amount to some tenths of degrees if a increases at lower temperatures, so that the boiling-point may perhaps be rounded off to 4°.5 K.

The triple-point pressure if it exists lies undoubtedly below 1 cm., perhaps also below 7 mm. According to the law of corresponding states the temperature can be estimated at about 3° K at this pressure. The viscosity of the liquid is still very slight at this temperature. If the helium should behave like pentane, we could descend to below 1,5° K before it became viscous, and still lower near 1° K before it became solid. How large the region of low temperatures (and high vacua) is that has now been opened, is, however, still to be investigated.

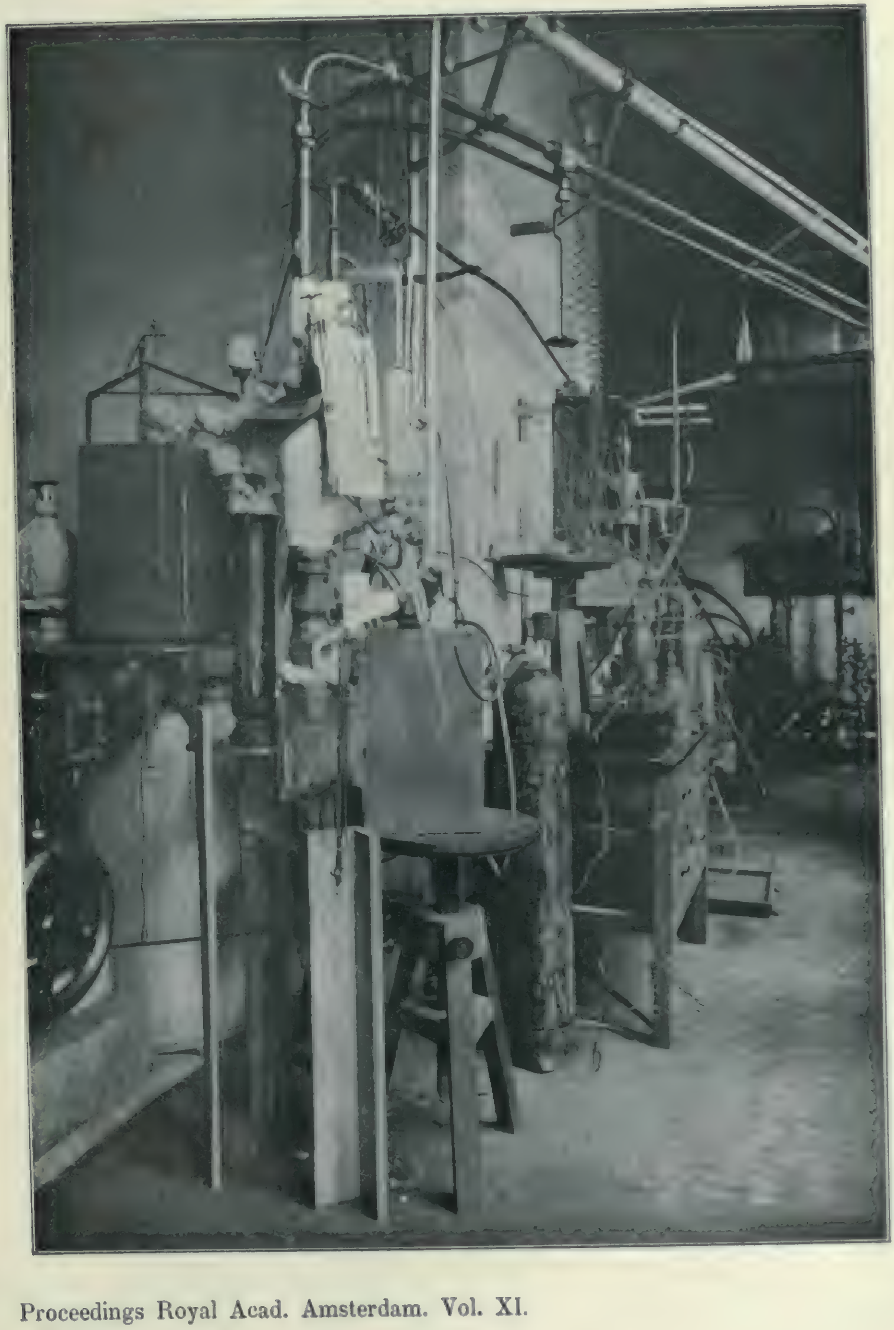
Liquid helium has a very slight density, viz. 0.15. This is smaller than was assumed and gives also a considerably higher value of b than can be derived from the isotherms at — 252°.72 and — 258°.82 now that the points mentioned in § 1 have been determined, viz. about 0.0007 provisionally. The value of b which follows from the liquid state is about double the value of b which was expected [viz. 0,0005], and was assumed in the calculations of Dr. Keesom and myself on mixtures of helium and hydrogen (Comp. Suppl. N°. 16 Sept. '07 § 1 fn. 5).

From the high value of b follows immediately a small value of the critical pressure, which probably lies in the neighbourhood of 2 or 3 atms., and is exceedingly low in comparison with that for other substances. So when helium is subjected to the highest pressures possible, the "reduced" pressures become much higher than are to be realized for any other substance. What may be obtained in this respect, by exerting a pressure of 5000 atms. on helium exceeds what would be reached when we could subject carbonic acid e.g. to a pressure of more than 100.000 atms.

The ratio of the density of the vapour and that of the liquid is

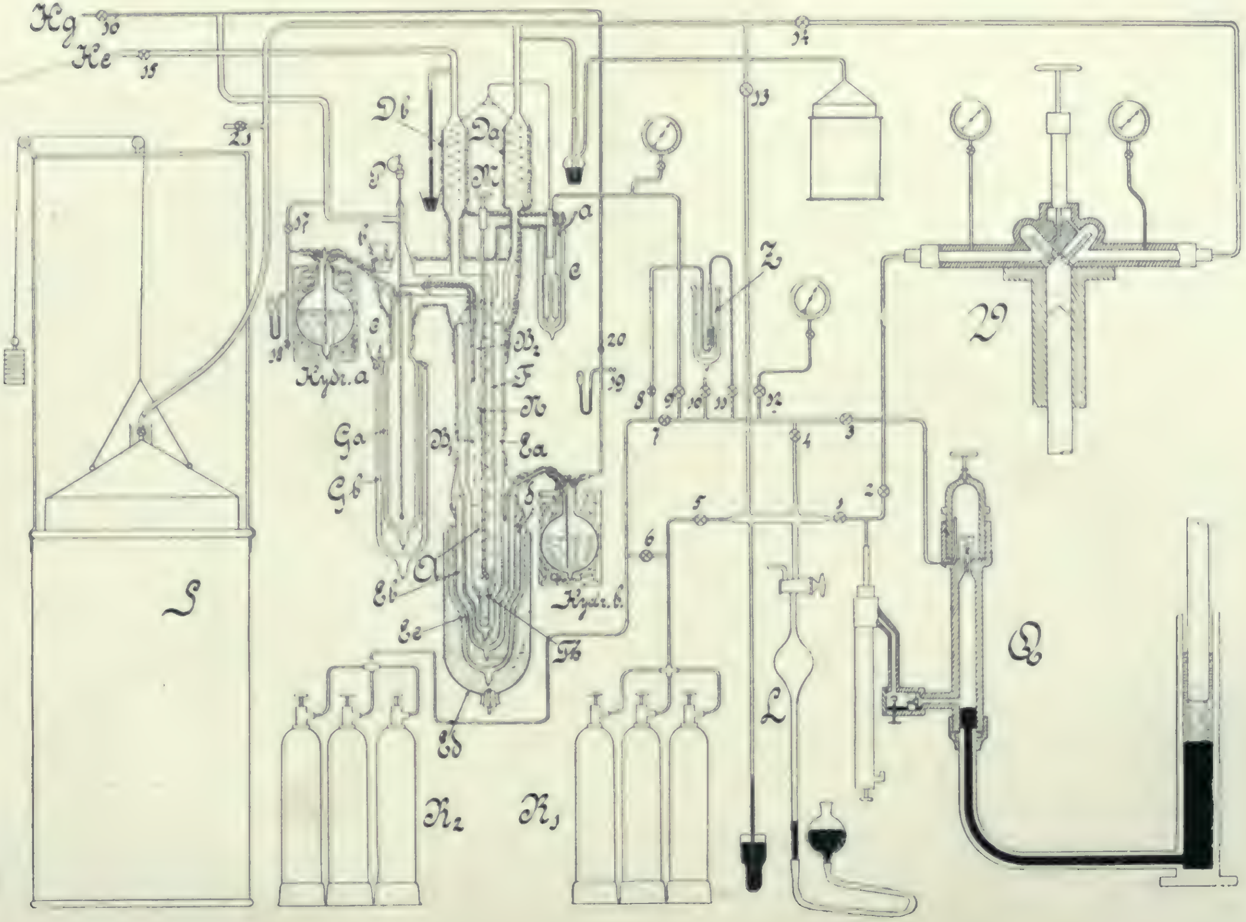
H. KAMERLINGH ONNES. "The liquefaction of helium."

Plate I.



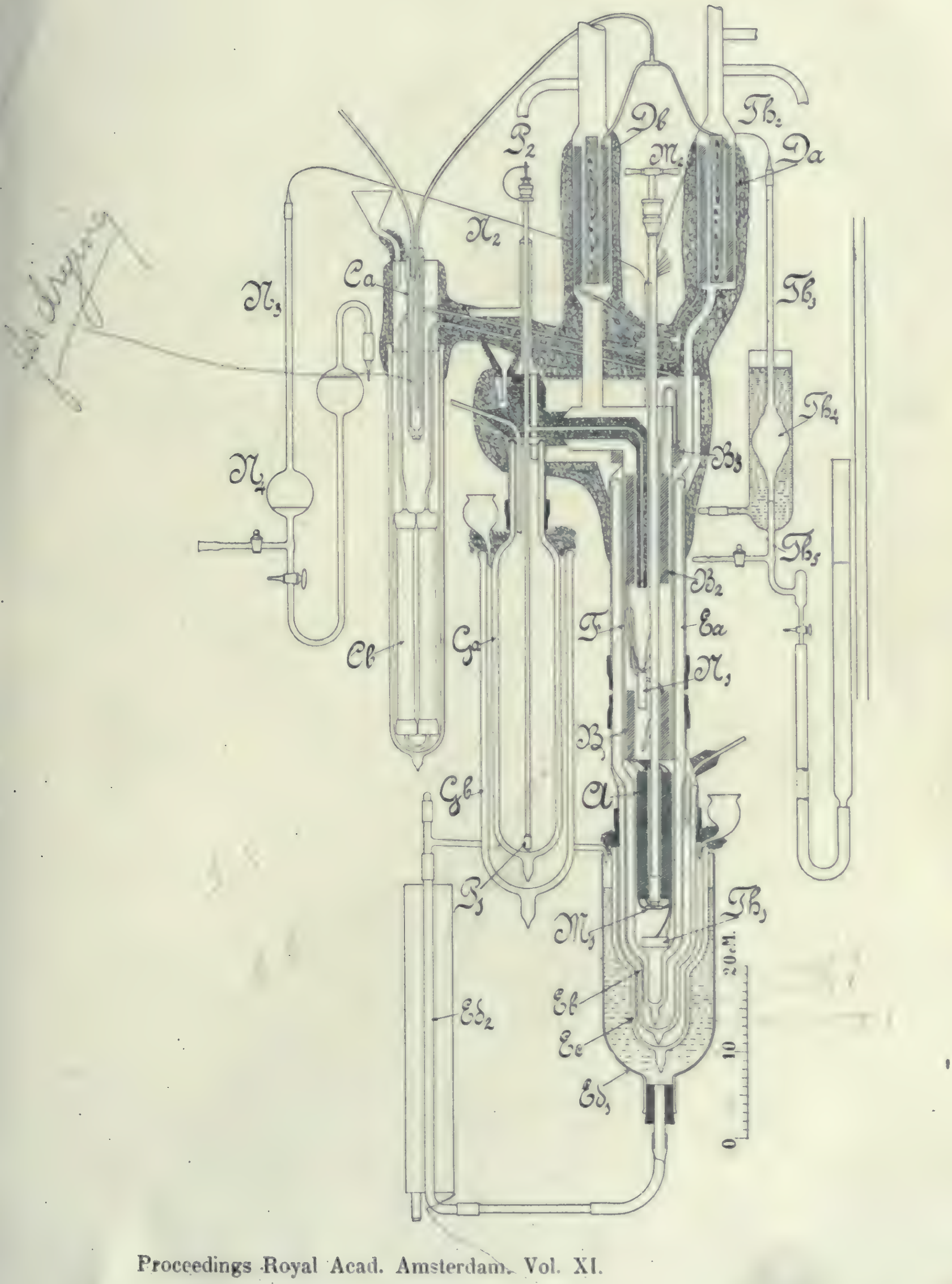
H. KAMERLINGH ONNES. "The liquefaction of helium."

Plate II.



H. KAMERLINGH ONNES. "The liquefaction of helium."

Plate III.



Proceedings Royal Acad. Amsterdam. Vol. XI.

about 1 to 11 at the boiling-point. It points to a critical temperature which is not much higher than 5° K., and a critical pressure which is not much higher than 2,3 atms.

But all the quantities mentioned will have to be subjected to further measurements and calculations before they will be firmly established, and before definite conclusions may be drawn from them.

We may only still mention here a preliminary value of a, viz. 0.00005. When in 1873 VAN DER WAALS in his Dissertation considered whether hydrogen would have an a, it was only after a long deliberation that he arrived at the conclusion that this must exist, even though it should be very small. It may be presumed that matter will always have attraction, was his argument, and as chance would have it these words were repeated by him in reference to helium some days before the liquefaction of helium (These Proc. June 1908). The a found now denotes the smallest degree of this attraction of matter, which still manifests itself with remarkable clearness also in helium in its liquefaction.

Geology. — "*The age of the layers of Sondé and Trinil on Java*".

By Prof. K. MARTIN.

(This paper will not be published in this Proceedings).

(September 8, 1908).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETINGS
of Saturday September 26, 1908.

(Translated from: Verslag van de gewone vergaderingen der Wis- en Natuurkundige Afdeeling van Zaterdag 26 September 1908, Dl. XVII).

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Physics. — "*Contribution to the theory of binary mixtures.*" VIII.
By Prof. J. D. VAN DER WAALS.

THE INTERSECTION OF THE CURVE $\frac{d^2p}{dv\,dx}=0$ WITH $\frac{dp}{dv}=0$.

By the aid of the approximate equation of state the course of the curve $\frac{d^2p}{dv\,dx}=0$ is given by the equation:

$$\frac{MRT\dfrac{db}{dx}}{(v-b)^2}=\frac{\dfrac{da}{dx}}{v^2}.$$

As has been observed before, it has a course which is analogous to that of the curve $\frac{dp}{dx}=0$. At given value of T it has an asymptote for that value of x, for which in rarefied gas state, the deviation from the law of BOYLE is maximum, viz. for which $MRT\frac{db}{dx}=\frac{da}{dx}$.

It has minimum volume on the line $v-b=3\frac{db}{dx}\frac{\frac{da}{dx}}{\frac{d^2a}{dx^2}}$, whereas the line $\frac{dp}{dx}=0$ has such a minimum volume on the line $v-b=2\frac{db}{dx}\frac{\frac{da}{dx}}{\frac{d^2a}{dx^2}}$.

The points of intersection of $\frac{d^2p}{dv\,dx}=0$ and $\frac{dp}{dx}=0$ indicate the points in which $\frac{dp}{dv}=0$ has a tangent parallel to the X-axis, as follows from $\frac{d^2p}{dv^2}\frac{dv}{dx}+\frac{d^2p}{dx\,dv}=0$. For such a point of intersection we have at the same time $\frac{MRT}{(v-b)^2}=\frac{2a}{v^3}$ and $\frac{MRT\frac{db}{dx}}{(v-b)^3}=\frac{\frac{da}{dx}}{v^3}$; and so $\frac{\frac{db}{dx}}{v-b}=\frac{\frac{da}{dx}}{2a}$, which last equation represents the locus of these points of intersection. Differentiating this locus "$v-b=2\frac{db}{dx}\frac{a}{\frac{da}{dx}}$" we find:

$$\frac{dv}{dx}=\frac{db}{dx}\frac{3\left(\frac{da}{dx}\right)^2-2a\frac{d^2a}{dx^2}}{\left(\frac{da}{dx}\right)^2}.$$

If in the diagram we think all the values of x present, e.g. ascending from the value of x for which $\frac{da}{dx}=0$, this locus is a curve with an asymptote for the value of x, for which $\frac{da}{dx}=0$, and it has a minimum volume for the value of x, for which $\left(\frac{da}{dx}\right)^2=\frac{2}{3}a\frac{d^2a}{dx^2}$. For greater values of x the volume increases.

If in $\frac{\frac{db}{dx}}{v-b}=\frac{\frac{da}{dx}}{2a}$ the value $3b$ is put for v, we find $\frac{1}{b}\frac{db}{dx}=\frac{1}{a}\frac{da}{dx}$.

But then not only $\frac{d^2p}{dv\,dx} = 0$ in the equation $\frac{d^2p}{dv^2}\frac{dv}{dx} + \frac{d^2p}{dv\,dx} = 0$, but also $\frac{d^2p}{dv^2}$. The value of $\frac{dv}{dx}$ is then indefinite, and at the temperature at which this takes place, and which is the minimum temperature represented by $\frac{8}{27}\frac{a_x}{b_x}$, the curve $\frac{dp}{dv}$ has two branches, which intersect in the point given by $v = 3b$ and x, belonging to $\frac{1}{b}\frac{db}{dx} = \frac{1}{a}\frac{da}{dx}$. For higher values of v, e.g. $v = 4b$, the point of intersection of the two curves lies on the vapour branch of $\frac{dp}{dv} = 0$, and vice versa. If we write $v = nb$, the form $\frac{2}{n-1} = \frac{\frac{1}{a}\frac{da}{dx}}{\frac{1}{b}\frac{db}{dx}}$ follows from $\frac{\frac{db}{dx}}{v-b} = \frac{\frac{da}{dx}}{2a}$. For those values of x for which the numerator is smaller than the denominator $n > 3$, and vice versa. Only if also $\frac{da}{dx} = 0$ should occur in the diagram, the value of n, and so also of v, is infinite.

If we determine the point in which the two curves touch, we shall find the same point in which $\frac{d^2p}{dv\,dx}$ has the minimum volume; for as the curve $\frac{dp}{dv} = 0$ has a tangent parallel to the X-axis in every point of intersection, also the curve $\frac{d^2p}{dv\,dx} = 0$ must have such a tangent in case of contact.

The condition that for a point of the last-mentioned curve $\frac{dv}{dx} = 0$ is $\frac{d^3p}{dv\,dx^2} = 0$. So we have

$$\frac{dp}{dv} = 0 \quad \text{or} \quad \frac{MRT}{(v-b)^2} = \frac{2a}{v^3}$$

$$\frac{d^2p}{dv\,dx} = 0 \quad \text{or} \quad \frac{MRT\frac{db}{dx}}{(v-b)^3} = \frac{\frac{da}{dx}}{v^3}$$

and

$$\frac{d^3p}{dv\,dx^2} = 0 \quad \text{or} \quad 3\frac{MRT\left(\frac{db}{dx}\right)^2}{(v-b)^4} = \frac{\frac{d^2a}{dx^2}}{v^3}$$

By comparing the square of the second of these equations with the product of the two others, we find back the condition:

$$\left(\frac{da}{dx}\right)^2 = \frac{2}{3}\,a\,\frac{d^2a}{dx^2}\,.$$

If we put $a = A + 2Bx + Cx^2$, in which $A = a_1$, $B = a_{12} - a_1$ and $C = a_1 + a_2 - 2a_{12}$, this equation leads to:

$$(B + Cx)^2 + \frac{B^2 - AC}{2} = 0$$

or

$$B + Cx = +\sqrt{\frac{a_1a_2 - a_{12}{}^2}{2}}\,.$$

The positive sign before the radical sign is required by the condition that $\frac{da}{dx}$ must be positive. If x is to be real, a_1a_2 must be $> a_{12}{}^2$, and the condition that x lies between 0 and 1 is indicated by the construction of fig. 33. Let OO' be the x-axis, and let PQ be

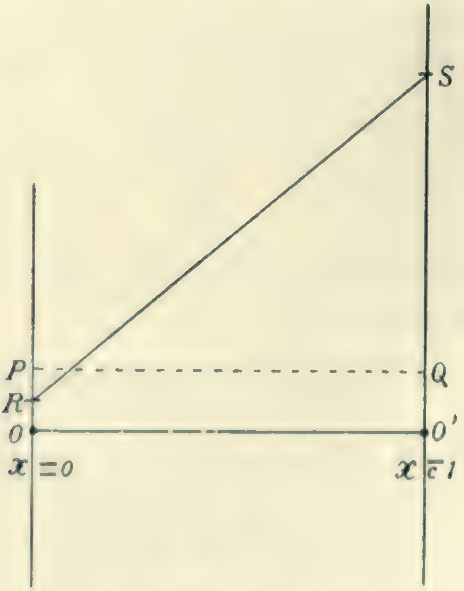

Fig. 33.

drawn at the height of $\sqrt{\frac{a_1a_2 - a_{12}{}^2}{2}}$. Let us then take $OR = a_{12} - a_1$ and $O'S = a_2 - a_{12}$, then the point of intersection of RS and

PQ will have to lie between $x=0$ and $x=1$ for the condition $\left(\frac{da}{dx}\right)^2=\frac{2}{3}a\frac{d^2a}{dx^2}$ to be fulfilled in the diagram.

According to the result arrived at in Contribution VII with regard to the point in which $\left(\frac{dp}{dx}\right)_v=0$ touches the line $\left(\frac{dp}{dv}\right)_x=0$, the value of x in which $\left(\frac{da}{dx}\right)^2=\frac{2}{3}a\frac{d^2a}{dx^2}$ must lie not very far from this point of contact.

But whether it might not even lie to the right of that value of x, for which $\frac{a_x}{b_x}$ has a minimum value, can only appear from a direct investigation. Then it may appear at the same time whether in case of contact of the two curves $\frac{dp}{dv}=0$ and $\frac{d^2p}{dvdx}=0$ the temperature has maximum value or minimum value.

Let us eliminate the value of v from the equations of the two curves. Among others we may do this by substituting the value of v from $\frac{2\frac{db}{dx}}{v-b}=\frac{1}{a}\frac{da}{dx}$ in $\frac{d^2p}{dv\,dx}=0$. Let us write:

$$\frac{v-b}{b}=2\frac{\frac{1}{b}\frac{db}{dx}}{\frac{1}{a}\frac{da}{dx}}=2z,$$

or

$$\frac{v}{b}=1+2z,$$

and

$$\frac{b}{v}\,\frac{1}{1+2z},$$

and

$$1-\frac{b}{v}=\frac{2z}{1+2z}.$$

From $\frac{d^2p}{dvdx}=0$ follows:

$$1-\frac{b}{v}=\sqrt[3]{\frac{MRT\frac{db}{dx}}{\frac{da}{dx}}}.$$

Hence:

$$\sqrt[3]{\frac{MRT\frac{db}{dx}}{\frac{da}{dx}}} = \frac{2z}{1+2z}.$$

Differentiating logarithmically, we get:

$$\frac{1}{3T}\frac{dT}{dx} - \frac{1}{3}\frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}} = \frac{1}{z}\frac{da}{dx}\frac{1}{1+2z}$$

Now

$$\frac{1}{z}\frac{dz}{dx} = \frac{1}{a}\frac{da}{dx} - \frac{1}{b}\frac{db}{dx} - \frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}}$$

or

$$\frac{1+2z}{3T}\frac{dT}{dx} - \frac{1}{3}\frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}}(1+2z) = \frac{1}{a}\frac{da}{dx} - \frac{1}{b}\frac{db}{dx} - \frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}}$$

or

$$\frac{1+2z}{3T}\frac{dT}{dx} + \frac{2}{3}\frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}}(1-z) = \frac{1}{a}\frac{da}{dx} - \frac{1}{b}\frac{db}{dx}$$

or

$$\frac{1+2z}{3T}\frac{dT}{dx} = \left[\frac{1}{a}\frac{da}{dx} - \frac{1}{b}\frac{db}{dx}\right]\left[1 - \frac{2}{3}\frac{a\frac{d^2a}{dx^2}}{\left(\frac{da}{dx}\right)^2}\right]$$

So the value $\frac{dT}{dx}$ is equal to 0, first if $\frac{1}{a}\frac{da}{dx} = \frac{1}{b}\frac{db}{dx}$, and secondly if $\left(\frac{da}{dx}\right)^2 = \frac{2}{3}a\frac{d^2a}{dx^2}$. If, when drawing T as function of x, we begin with small values of x, and if we should admit also negative values of x into our consideration, then both factors in the expression for $\frac{dT}{dx}$ are negative e. g. for $\frac{da}{dx} = 0$, and so $\frac{dT}{dx}$ is positive. If x increases a value of x is reached for which one of these factors becomes equal to 0. For still higher value of x the second factor becomes equal to 0. Between these two special values of x, $\frac{dT}{dx}$ is negative — and for values of x which are larger than that for which also the second factor is zero, $\frac{dT}{dx}$ is again positive. So the value of T presents a maximum and a minimum.

In general we must now put two cases as possible according as the value of x for which $\frac{1}{a}\frac{da}{dx}=\frac{1}{b}\frac{db}{dv}$, is smaller or larger than that for which $\left(\frac{da}{dx}\right)=\frac{2}{3}a\frac{d^2a}{dx^2}$. The intermediate case in which these two values would coincide, might be considered as a third possibility. Let us call the maximum value of the temperature T_M, and the minimum value T_m. For a value of T below T_m there is only one point of intersection of $\frac{dp}{dv}=0$ and $\frac{d^2p}{dvdx}=0$, namely at small value of x. For values of T above T_M there is also only one point of intersection for large value of x. But for values of T between T_m and T_M there are three points of intersection. Of these three points of intersection there is always one, the middle one, which lies at a value of x lying between that which makes the first factor equal to zero, and that which makes the second factor equal to zero.

To give a survey of the course of the points of intersection of $\frac{dp}{dv}=0$ and $\frac{d^2p}{dvdx}=0$ at different temperatures, and so of the circumstances for which $\frac{dp}{dv}=0$ has a maximum or minimum volume, we shall have to separately treat the cases for the different situation of the two values of x, for which $\frac{1}{a}\frac{da}{dx}=\frac{1}{b}\frac{db}{dx}$, and $\left(\frac{da}{dx}\right)^2=\frac{2}{3}a\frac{d^2a}{dx^2}$.

Let us first take the case for which the value of x for minimum value of $\frac{a_x}{b_x}$ is the smallest. This case is the simplest, and was discussed by me already before. Then a curve $\frac{d^2p}{dvdx}=0$ indicated in fig. 34 by α, passes through the double point of $\frac{dp}{dv}=0$. For lower T, α has assumed the position β, and $\frac{dp}{dv}=0$ the position γ, so that there are then two points of intersection (1 and 2) to be found.

But at higher T these points of intersection exist no longer; then the line $\frac{d^2p}{dvdx}=0$ runs between the two branches in which $\frac{dp}{dv}=0$ has split up, without intersecting them, at least at this place. There

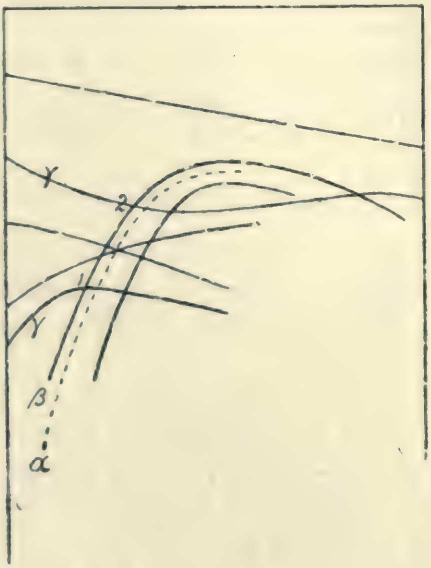

Fig. 34.

is, however, still a point of intersection, but at much greater value of x, namely a point of intersection formed by the branch of $\frac{d^2p}{dvdx}=0$ which runs again to larger volumes. In this point of intersection the righthand branch of $\frac{dp}{dv}=0$ has again minimum volume. So for values of T below that of the double point of $\frac{dp}{dv}=0$, the branch of the liquid volumes of $\frac{dp}{dv}=0$ has two points of intersection with $\frac{d^2p}{dvdx}=0$, so a maximum and a minimum volume, and for much smaller value of x there is then a minimum volume on the vapour branch. If we lower T still further, maximum and minimum volume of the liquid branch draw nearer to each other, and they coincide at the value of x for which $\left(\frac{da}{dx}\right)^2=\frac{2}{3}a\frac{d^2a}{dx^2}$. Then the vapour branch has two coinciding values of x, for which $\frac{dv}{dx} = 0$, and so also a point of inflection, namely for the volume that is the smallest volume for which a point of intersection of the two curves exists. At still lower temperature the liquid branch has no longer a point of intersection; but the point of intersection of the vapour branch continues to exist, and proceeds continually to smaller value of x. I need hardly point out that in this description negative values of x are again not considered as unreal. The condition for a point occurring on the curve $\frac{dp}{dv} = 0$ in which $\frac{dv}{dx} = 0$ and $\frac{d^2v}{dx^2} = 0$ is found from:

$$\frac{d^2p}{dv^2}\frac{dv}{dx} + \frac{d^2p}{dvdx} = 0$$

and

$$\frac{d^2p}{dv^2}\frac{d^2v}{dx^2} + \frac{d^3p}{dv^3}\left(\frac{dv}{dv}\right)^2 + 2\frac{d^3p}{dvdx}\left(\frac{dv}{dx}\right) + \frac{d^3p}{dvdx^2} = 0.$$

Hence besides $\frac{dp}{dv} = 0$, also $\frac{d^2p}{dvdx} = 0$ and $\frac{d^3p}{dvdx^2} = 0$.

Let us now consider the second case, for which the value of x corresponding to $\left(\frac{da}{dx}\right)^2 = \frac{2}{3}a\frac{d^2a}{dx^2}$, is the smallest. For this value of x the value of T is then maximum, and the temperature for the double point of $\frac{dp}{dv} = 0$ will be a minimum. This means that with decrease of T two points of intersection *vanish*, whereas in the preceding case two new points of intersection *appear* with decrease of T.

Let us first consider this minimum temperature; then a curve $\frac{d^2p}{dvdx} = 0$ passes through the double point, which, in this point, may be considered to have two points in common with the line $\frac{dp}{dv} = 0$, and which has a third point of intersection for smaller value of x. This third point of intersection is to be found on the vapour branch of the lefthand branch of $\frac{dp}{dv} = 0$, because it has smaller x. Fig. 35 indicates the places of the three points of intersection for this value of T. With decrease of T two of the points of intersection lie on the vapour branch of the lefthand branch of the line $\frac{dp}{dv} = 0$, and a third point of intersection on the liquid branch of the other branch. With increase of T the two points of intersection on the left-hand branch coincide in the point for which x is found from $\left(\frac{da}{dx}\right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}$. Everything shows that at the temperature of the double point that part of the line $\frac{d^2p}{dvdx} = 0$ runs through the double point that lies beyond the minimum volume. With T lower than that of the double point this part of the curve remains entirely in the unstable region.

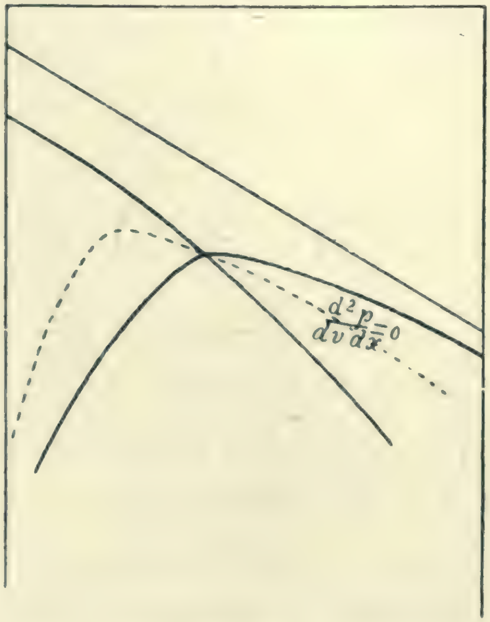

Fig. 35.

If we try to ascertain on what it depends whether the value of x which corresponds to $\frac{1}{a}\frac{da}{dx} = \frac{1}{b}\frac{db}{dx}$ is smaller or larger than that for which $\left(\frac{da}{dx}\right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}$ we may, to decide this, substitute the value of x which follows from the second of these equations, in:

$$b\frac{da}{dx} - a\frac{db}{dx}.$$

If we then find a positive value for this form, the first case holds; then the point where $\left(\frac{da}{dx}\right)^2 = \frac{2}{3} a \frac{d^2a}{dx^2}$ lies in the region where the value of $\frac{a}{b}$ again increases.

Eliminating a we may also write for $b\frac{da}{dx} - a\frac{db}{dx}$:

$$\frac{da}{dx}\left\{ b - \frac{3}{2}\frac{db}{dx}\frac{\frac{da}{dx}}{\frac{d^2a}{dx^2}} \right\}$$

and as $\frac{da}{dx}$ must be positive, just as $\frac{d^2a}{dx^2}$, the sign depends on:

$$\frac{2}{3}\, b \frac{d^2a}{dx^2} - \frac{3}{2}\frac{db}{dx}\frac{da}{dx}.$$

And if we put $b_2 = nb_1$, $a = A + 2Bx + Cx^2$, this form becomes:

$$\frac{2}{3} C\,[1 + (n-1)\,x] - (n-1)\,[B + Cx]$$

or

$$\frac{2}{3} C + \frac{2}{3}(n-1)\,Cx - (n-1)\,(B + Cx)$$

or

$$\frac{2}{3}\frac{C}{n-1} - \frac{2}{3} B - \frac{B+Cx}{3}$$

Now we have found above $B + Cx = +\sqrt{\frac{a_1a_2 - a^2_{12}}{2}}$, and as $B = a_{12} - a_1$ and $C = a_1 + a_2 - 2a_{12}$, the sign depends on:

$$\frac{a_1 + a_2 - 2a_{12}}{n-1} - (a_{12} - a_1) - \frac{1}{2}\sqrt{\frac{a_1a_2 - a^2_{12}}{2}}.$$

If this sign is positive we have the case treated first. So for this case

$$\frac{(a_2 - a_{12}) - (a_{12} - a_1)}{a_{12} - a_1} > n - 1$$

or

$$\frac{a_2 - a_{12}}{a_{12} - a_1} > n.$$

is certainly necessary, but not sufficient.

With the following numerical values the conditions necessary for the first case, and the condition that the two values of x occur in the diagram, are satisfied.

Let $n=5$, $a_1=1$, $a_2=30$ and $a_{12}=2$. The value of x satisfying $\left(\frac{da}{dx}\right)^2=\frac{2}{3}a\frac{d^2a}{dx^2}$, is found from:

$$(a_{12}-a_1)+(a_1+a_2-2a_{12})x=\sqrt{\frac{a_1a_1-a_{12}^2}{2}}$$

or

$$1+27x=\sqrt{13}=3,6$$

or

$$x_1=\frac{2,6}{27}.$$

The value of x satisfying $\frac{1}{a}\frac{da}{dx}=\frac{1}{b}\frac{db}{dx}$, is found from the equation:

$$B-\frac{n-1}{2}A+Cx+\frac{n-1}{2}Cx^2$$

or

$$-1+27x+54x^2=0$$

or

$$x_2=0,035.$$

If we had put $a_2=10$, leaving the other values unchanged, so that $\frac{a_2-a_{12}}{a_{12}-a_1}>n$ still remains larger than x, we find x_1 from the equation:

$$1+7x_1=\sqrt{3} \quad \text{and} \quad x_1=0,1045$$

and x_2 from the equation:

$$-1+7x_2+14x_2^2=0$$

or

$$x_2=-\frac{1}{4}+\sqrt{+\frac{1}{14}}$$

$$4x_2=-1+\sqrt{\frac{15}{7}} \quad \text{and} \quad x_2=0,116$$

And finally, let us take a numerical example, more in agreement with those which occur in the cases of minimum plaitpoint temperature studied experimentally. Let $n=1,5$, $a_1=1$, $a_2=1,45$, so that $T_{k_2}<T_{k_1}$. Let further $a_{12}=1,1$. Then x_1 is found from the equation:

$$0,1+0,25x=\sqrt{0,12}=0,3435\ldots.$$

$$x_1=0,974$$

and x_2 from the equation:

$$-0{,}15 + 0{,}25x + \frac{1}{4}\,0{,}25\,x^2 = 0$$

or x_1 nearly equal to 0,5.

Here we very clearly get back the first case.

The intermediate case would require that x_1 should be equal to x_2. If we wish to direct our attention to other particularities of the intermediate case, we observe: 1. that then there is only one point of intersection for $\frac{dp}{dv} = 0$ and $\frac{d^2p}{dvdx} = 0$ at every temperature; 2. that then at the double point of $\frac{dp}{dv} = 0$ one of the branches must have a tangent parallel to the X-axis; and so, the two values of $\frac{dv}{dx}$ for that double point being given by the equation:

$$\frac{d^3p}{dv^3}\left(\frac{dv}{dx}\right)^2 + 2\,\frac{d^3p}{dv^2dx}\left(\frac{dv}{dx}\right) + \frac{d^3p}{dvdx^2} = 0$$

$\frac{d^3p}{dvdx^2}$ is again equal to zero (see page 195). The curve $\frac{d^2p}{dvdx} = 0$ now does not pass through the double point either with its descending, nor with its ascending branch, but has there minimum volume. At lower temperature the vapour branch of $\frac{dp}{dv} = 0$ is cut in a point with somewhat lower value of x, and at higher temperature the liquid branch of the righthand branch is intersected with slightly higher value of x. Just at the temperature of the double point $\frac{d^2p}{dvdx} = 0$ touches with a tangent parallel to the X-axis.

If more in general, we wish to determine what the ratio of

$$\frac{\left(\frac{da}{dx}\right)^2}{a\,\frac{d^2a}{dx^2}} = m$$

is at that value of x for which $\frac{a_x}{b_x}$ has minimum value, we may take the following course. From:

$$b\,\frac{da}{dx} = a\,\frac{db}{dx}$$

we derive:

$$[1 + (n-1)\,x]\,[B + Cx] = \frac{n-1}{2}\,(A + 2Bx + Cx^2)$$

or

$$x^2 + \frac{2}{n-1} x + \frac{\frac{2}{n-1} B - A}{C} = 0$$

and so

$$x = - \frac{1}{n-1} + \sqrt{\left[\frac{1}{(n-1)} - \frac{B}{C}\right]^2 + \frac{AC-B^2}{C^2}}$$

From $\left(\frac{da}{dx}\right)^2 = ma \frac{d^2a}{dx^2}$ we derive:

$$(2-m)(B + Cx)^2 = m(AC - C^2)$$

or

$$x + \frac{B}{C} = \sqrt{\frac{m}{2-m} \frac{AC-B^2}{C^2}}$$

By equating the two values of x thus obtained, we find the equation:

$$\frac{B}{C} - \frac{1}{n-1} + \sqrt{\left[\frac{1}{(n-1)^2} - \frac{B}{C}\right]^2 + \frac{AC-B^2}{C^2}} = + \sqrt{\frac{m}{2-m} \frac{AC-B^2}{C^2}}$$

from which follows:

$$\frac{AC-B^2}{C^2} = + 2\left[\frac{1}{n-1} - \frac{B}{C}\right] \sqrt{\frac{m}{2-m} \frac{AC-B^2}{C^2}} + \frac{m}{2-m} \frac{AC-B^2}{C^2}$$

or

$$\frac{1-m}{2-m} \sqrt{\frac{AC-B^2}{C^2}} = \left[\frac{1}{n-1} - \frac{B}{C}\right] \sqrt{\frac{m}{2-m}}$$

or

$$\frac{1-m}{\sqrt{m(2-m)}} \sqrt{\frac{AC-B^2}{C^2}} = \frac{1}{n-1} - \frac{1}{\frac{a_2-a_{12}}{a_{12}-a_1} - 1} = \frac{\frac{a_2-a_{12}}{a_{12}-a_1} - n}{(n-1)\left(\frac{a_2-a_{12}}{a_{12}-a_2} - 1\right)}$$

or

$$\frac{1-m}{\sqrt{m(2-m)}} \frac{\sqrt{(a_1a_2-a_{12}^2)}}{a_{12}-a_1} = \frac{\frac{a_2-a_{12}}{a_{12}-a_1} - n}{n-1}$$

In particular it appears that $m = 1$, if $\frac{a_2-a_{12}}{a_{12}-a_1} = n$; and if $\frac{a_2-a_{12}}{a_{12}-a_1}$ should be $\gtrless n$, then $m \lesseqgtr 1$, at least if $a_{12} > a_1$.

If m is known for certain value of x, the decrease or increase of m may be derived from the equation:

$$(2-m)\, a = \text{constant},$$

which constant is equal to zero, if $a_1a_2 = a_{12}^2$, and has else the sign of $a_1a_2-a_{12}^2$.

Physics. — "*Contribution to the theory of binary mixtures.*" IX. By Prof. J. D. VAN DER WAALS.

THE INTERSECTION OF $\left(\frac{dp}{dx}\right)_v = 0$ AND $\left(\frac{d^2\psi}{dx^2}\right)_v = 0$.

As in previous communications we shall write the equation of $\left(\frac{dp}{dx}\right)_v = 0$ in the form $\frac{MRT}{(v-b)^2}\frac{db}{dx} = \frac{da}{dx}\frac{1}{v^2}$, and the equation of $\left(\frac{d^2\psi}{dx^2}\right)_v = 0$ in the form:

$$MRT\left\{\left(\frac{1}{x(1-x)}\right) + \left(\frac{db}{dx}\right)^2 \frac{1}{(v-b)^2}\right\} = \frac{\frac{d^2a}{dx^2}}{v}.$$

Then the locus of the points of intersection is given by the equation:

$$(v-b)^2 + \left(\frac{db}{dx}\right)^2 x(1-x) = x(1-x)\frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}}\, v\, \frac{db}{dx}$$

or

$$(v-b)^2 - x(1-x)\frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}}\frac{db}{dx}(v-b) + x(1-x)\left[\frac{db}{dx} - b\frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}}\right] = 0.$$

The factor of the known term of this equation: $\frac{\frac{db}{dx}\frac{da}{dx} - b\frac{d^2a}{dx^2}}{\frac{da}{dx}}$ may be written in the form:

$$\frac{db}{dx}\,\frac{B - \frac{C}{n-1}}{B + Cx},$$

if $b = b_1(1-x) + b_2x$, and $a = A + 2Bx + Cx^2$ be put, and the equation itself may be given in the form:

$$\frac{(v-b)^2}{\left(\frac{db}{dx}\right)^2} - x(1-x)\frac{C}{B+Cx}\frac{(v-b)}{\frac{db}{dx}} + x(1-x)\frac{B - \frac{C}{n-1}}{B+Cx} = 0.$$

When $B - \frac{C}{n-1}$ is negative, this equation has certainly a positive root, when viz. the quantity $B + Cx$ is positive, which is required for the occurrence of the line $\left(\frac{dp}{dx}\right)_v = 0$. The negative root is without significance for the problem. The quantity $\left(\frac{C}{n-1} - B\right)$ positive may be written as follows:

$$(a_{12} - a_1) \frac{\frac{a_2 - a_{12}}{a_{12} - a_1} - n}{n-1} > 0.$$

Let us call the case $\frac{a_2 - a_{12}}{a_{12} - a_1} < n$ the first case, and $\frac{a_2 - a_{12}}{a_{12} - a_1} > n$ the second case.

In the first case the quadratic equation in $\frac{v-b}{\frac{db}{dx}}$ has the factor of the first power of $(v-b)$ negative, and the known term positive. Two real positive values of $v-b$ can then satisfy this equation. These roots are however real only if:

$$x^2 (1-x)^2 \left(\frac{C}{B+Cx}\right)^2 \geqq 4x(1-x) \frac{B - \frac{C}{n-1}}{B+Cx},$$

or

$$x(1-x) \geqq \left(\frac{B}{C} - \frac{1}{n-1}\right) \frac{B+Cx}{C}.$$

So the roots are imaginary if:

$$x^2 - x \left\{1 - 4\left(\frac{B}{C} - \frac{1}{n-1}\right)\right\} + 4\frac{B}{C}\left(\frac{B}{C} - \frac{1}{n-1}\right) > 0.$$

For values of x which are nearly 0 or nearly 1, they are therefore imaginary. From this follows that the locus of the points of intersection of $\left(\frac{dp}{dx}\right)_v = 0$ and $\left(\frac{d^2\psi}{dx^2}\right)_v = 0$ is a closed curve in the first case. By dividing by $x(1-x)$ we have only lost the values $x = 0$ and $x = 1$, which, however, only correspond to $v - b = 0$ and $T = 0$. This closed curve can contract to a single point, and even disappear altogether. Contraction to a single point takes place, if:

$$\left\{1-4\left(\frac{B}{C}-\frac{1}{n-1}\right)\right\}^2=16\,\frac{B}{C}\left(\frac{B}{C}-\frac{1}{n-1}\right),$$

or if

$$1-8\left(\frac{B}{C}-\frac{1}{n-1}\right)-\frac{16}{n-1}\left(\frac{B}{C}-\frac{1}{n-1}\right)=0,$$

or

$$\frac{B}{C}-\frac{1}{8}\,\frac{(n+3)^2}{n^2-1},$$

or

$$\frac{a_2-a_{12}}{a_{12}-a_1}=1+8\,\frac{n^2-1}{(n+3)^2},$$

or

$$\frac{a_2-a_{12}}{a_{12}-a_2}-n=-(n-1)\left\{1-\frac{8\,(n+1)}{(n+3)^2}\right\}.$$

In this expression the value of the factor $n-1$ always lies between 0 and 1 for values of n between 1 and ∞. For values of $\frac{a_2-a_{12}}{a_{12}-a_2}<1+8\,\frac{n^2-1}{(n+3)^2}$ the locus is imaginary.

The point at which the locus disappears, lies at $x=\frac{n+3}{(4n+1)}$ and so always between $\frac{1}{2}$ and $\frac{1}{4}$, and at $v-b=\frac{\frac{db}{dx}}{4}\,\frac{n-1}{n+1}$ or $v=\frac{b_1+b_2}{2}$. By substitution in $\left(\frac{dp}{dx}\right)_v=0$ we find the value of MRT equal to:

$$MRT=\frac{(a_1+a_2-2a_{12})}{b_2-b_1}\,\frac{(n-1)^3\,(n+3)\,(3n+1)}{16\,(n+1)^5}.$$

This is not the point in which the curve $\frac{d^2\psi}{dx^2}=0$ disappears. Already the circumstance that the latter curve disappears between $x=\frac{1}{3}$ and $x=\frac{1}{2}$, whereas in the same cases the discussed point disappears between $x=\frac{1}{4}$ and $x=\frac{1}{2}$, shows this. We may, however conclude, from this, that as n draws nearer to 1, the two points will approach each other as regards the value of x.

Thus (cf. Contribution III These Proc. IX p. 829) $x_g=0{,}48$ for $\frac{1}{n-1}=5.04$, whereas with $x=\frac{n+3}{4(n+3)}$ nearly 0.477 is found. But the value of v is much smaller for the point discussed here than for the point in which the curve $\frac{d^2\psi}{dx^2}=0$ disappears.

We should have to expect à priori that these two points differ. Let us imagine $\frac{d^2\psi}{dx^2}=0$ for different values of T as a surface with the axes x, v and T, and let the T-axis be the vertical axis. Then this is a surface with the whole v,x-plane as basis, with top at $T=T_g$. Let us also imagine $\frac{dp}{dx}=0$ as surface construed on the same axes, then the sections of this surface pass to larger x and larger v with ascending values of T. Now this latter surface cannot pass through the top of $\frac{d^2\psi}{dx^2}=0$ without yielding other points of intersection, a curve of intersection. If it can touch in the top, then it would be possible that this curve of intersection did not exist. But a tangent plane to $\frac{d^2\psi}{dx^2}=0$ runs parallel to the x,v-plane, and and such a tangent plane $\frac{dp}{dx}=0$ has not.

That a tangent plane in the top of $\frac{d^2\psi}{dx^2}=0$ runs parallel to the x,v-plane, follows from:

$$\frac{d^3\psi}{dx^2dT}\,dT+\frac{d^3\psi}{dx^3}\,dx+\frac{d^3\psi}{dx^2dv}\,dv=0.$$

In the top $\frac{d^3\psi}{dx^3}$ and $\frac{d^3\psi}{dx^2dv}$ are both equal to zero, whereas $\frac{d^3\psi}{dx^2dT}$ is not equal to 0; hence $\frac{dT}{dx}$ and $\frac{dT}{dv}$ is zero, or the tangent plane parallel to the v,x-plane.

As soon as $\frac{a_2-a_{12}}{a_{12}-a_1}$ is not only smaller than n, but also smaller than $1+8\frac{n^2-1}{(n+3)^2}$, the two curves do not intersect at any temperature. If on the other hand $\frac{a_2-a_{12}}{a_{12}-a_1}<n$, and $>1+8\frac{n^2-1}{(n+3)^2}$, the two surfaces $\frac{d^2\psi}{dx^2}=0$ and $\frac{dp}{dx}=0$ intersect in such a way that the projection of the section is a closed curve; the section itself lies then on the side of the small volumes of $\frac{d^2\psi}{dx^2}=0$, and between two low temperatures. If we denote these temperatures by T_1 and T_2, then contact does not begin before T_1; between T_1 and T_2 there is intersection, and at T_2 there is again contact. So at T_1 the curve $\frac{dp}{dx}=0$ proceeds more rapidly towards larger volumes with rise of temperature, but at T_2 on the contrary, the curve $\frac{d^2\psi}{dx^2}=0$.

In agreement with fig. 24 (Contribution V p. 134) the value of x for the minimum volume of $\frac{dp}{dx}=0$ is then smaller than that of the points of contact; and the point to which the locus of the points of contact contracts lies then on that portion of $\frac{dp}{dx}=0$ that proceeds to greater volumes with increasing x.

We may verify this by showing that $\left(\frac{d^2p}{dx^2}\right)_v$ is *positive* for this point. As $\left(\frac{d^2p}{dx^2}\right)_v = 2\frac{MRT\left(\frac{db}{dx}\right)^2}{(v-b)^3} - \frac{\frac{d^2a}{dx^2}}{v^2}$, for a point of $\left(\frac{dp}{dx}\right)_v$, or for which $\frac{MRT\frac{db}{dx}}{(v-b)^2}=\frac{\frac{da}{dx}}{v^2}$, the sign of $\left(\frac{d^2p}{dx^2}\right)_v$ will depend on:

$$\frac{\frac{db}{dx}}{v-b}-\frac{1}{2}\frac{\frac{d^2a}{dx^2}}{\frac{da}{dx}}$$

or on

$$\frac{\frac{da}{dx}}{\frac{d^2a}{dx^2}}-\frac{1}{2}\frac{v-b}{\frac{db}{dx}}$$

or on

$$\left(\frac{B}{C}+x\right)-\frac{1}{2}\frac{v-b}{\frac{db}{dx}}$$

If, as was found above, we take $\frac{B}{C}=\frac{1}{8}\frac{(n+3)^2}{n^2-1}$ and $x=\frac{n+3}{4(n+1)}$

and so $\frac{B}{C}+x=\frac{1}{8}\,\frac{(n+3)\,(3n+1)}{n^2-1}$, while $\frac{1}{2}\,\frac{v-b}{\frac{db}{dx}}=\frac{1}{8}\,\frac{n-1}{n+1}$, it is at once evident that the sign is certainly positive.

We can now get an insight into the way in which increase of the value of $\frac{a_2-a_{12}}{a_{12}-a_2}$ influences the intersection of the two surfaces $\frac{d^2\psi}{dx^2}=0$ and $\frac{dp}{dx}=0$. If this quantity, which I shall represent by k, is smaller than $1+8\,\frac{n^2-1}{(n+3)^2}$, no intersection is possible. In this consideration we shall leave n and C invariable, and so keep $\frac{d^2\psi}{dx^2}=0$ unchanged. If we now make k increase, $\frac{dp}{dx}=0$ will vary and intersect the surface $\frac{d^2\psi}{dx^2}=0$. When $k<n$, this intersection takes place in a closed curve. As well in the v,x-projection as in the T,x-projection and in the v,T-projection we may speak of a lower and an upper branch. But these branches do not extend over the whole width from $x=0$ to $x=1$. With approach of k to n the width of this section becomes larger, but the lower branch descends continually, and the upper branch ascends. In the v,x-projection this implies that the branch with the lower value of v approaches b, and that the upper branch assumes a higher value of v. In the T,x-projection this means that T verges to zero for the lower branch, and increases for the upper branch, but still remains very far below the value of T_q (See Contribution III These Proc. IX p. 830). And finally when k has become equal to n, the closed curve of the section extends from $x=0$ to $x=1$, but the lower branch coincides with the line $v=b$, and the value of T for this branch is the absolute zero-point. For the upper branch v and T have constantly increased. And the question rises whether then the whole section is still found on what I shall call the back side for the surface $\frac{d^2\psi}{dx^2}=0$; i.e. the points with the smaller value of v. We shall presently revert to this question. But already now it is to be seen what will be the consequence of increase of k above n.

The process we described above, goes on. The lower branch does not become imaginary, but has values of $v<b$ and values of T which are again positive. So they are of no importance for the real

problem; and as soon as $k > n$ we have only to occupy ourselves with a single branch for the section. This is also immediately seen from the quadratic equation in $v-b$ of p. 201, which has then one negative, and one positive root. So if $k > n$, we may say that the two surfaces intersect in a curve which has only one branch. For $x=0$ and $x=1$ the value of v is always equal to b, and that of T always equal to 0. From this follows already that there will be question of a maximum value of T for the section. For this value of T the two curves will touch at given value of T, viz. $\left(\frac{d^2\psi}{dx^2}\right)_{vT}=0$ and $\left(\frac{dp}{dx}\right)_{vT}=0$. We have also met with such a contact in the case $k < n$, and we then concluded that the contact took place as is represented in fig. 24^c (Contribution V p. 134).

But another contact is possible, namely such a contact for which the curve $\left(\frac{d^2\psi}{dx^2}\right)_{vT}=0$ lies in the region where $\left(\frac{dp}{dx}\right)_{vT}$ is positive everywhere except at the point of contact, or as we might also express it, outside $\left(\frac{dp}{dx}\right)_{vT}=0$. This would imply for the intersection of the two surfaces, that the common curve which runs upwards from $x=0$, and $x=1$ and $T=0$, passes round the top of $\left(\frac{d^2\psi}{dx^2}\right)_{vT}=0$, or that it remains entirely on the side of the small volumes, as was the case up to now.

In the gradual transformation of the common line of intersection which is due to the increase of k above n, it must, therefore, have passed through the top of $\frac{d^2\psi}{dx^2}=0$ for certain value of k. And we shall now treat the condition for this circumstance. Properly speaking I have already tried to solve this problem in Contribution III p. 834, to which I refer for the meaning of the following formula. The circumstance that the curve of intersection passes through the top is given by:

$$\frac{d^2a}{dx^2}(1-2x_g)=\frac{da}{dx}\,4y_g{}^2 .$$

But I shall adapt the discussion of this formula to the systematic treatment of this paper.

If we put the value $\frac{(1-2x_g)^2}{4x_g(1-x_g)}$ for $y_g{}^2$ (see Cont. III p. 832) this equation may assume the following form:

$$\frac{B}{C}=\frac{x_g\,(3x_g-1)}{1-2x_g}-\frac{1}{n-1}.$$

This equation may also be derived by the following consideration. If the top of $\frac{d^2\psi}{dx^2}=0$ is also to be a point of $\frac{dp}{dx}=0$, the following equations are to be satisfied: $\frac{d^2\psi}{dx^2{}_{vT}}=0$, $\frac{d^3\psi}{dx^3{}_{vT}}=0$, $\frac{d^3\psi}{dvdx^2}=0$, and $\frac{d^2\psi}{dxdv}=0$. It appears from this, that not only $\frac{dp}{dx}=0$ is to be satisfied but also $\frac{d^2p}{dx^2}=0$. This means that the point of the curve $\left(\frac{dp}{dx}\right)_{vT}=0$ at which this curve has its minimum volume, must pass through the top. So the following equations must be satisfied:

$$\frac{MRT\,\frac{db}{dx}}{(v-b)^2}=\frac{\frac{da}{dx}}{v^2}$$

and

$$2\,\frac{MRT\left(\frac{db}{dx}\right)^2}{(v-b)^3}=\frac{\frac{d^2a}{dx^2}}{v^2}$$

and so also

$$\frac{v-b}{2\,\frac{db}{dx}}=\frac{\frac{da}{dx}}{\frac{d^2a}{dx^2}}=\frac{B}{C}+x$$

Now for the top of $\frac{d^2\psi}{dx^2}=0$ (Contribution III p. 829) the equation

$$\frac{v-b}{2\left(\frac{db}{dx}\right)}=\sqrt[3]{\frac{x_g^2\,(1-x_g)^2}{4\,(1-2x_g}}\quad\text{en}\quad\frac{1}{n-1}=\frac{x_g^2}{1-2x_g}-\sqrt[3]{\frac{x_g^2\,(1-x_g)^2}{4\,(1-2x_g)}}$$

holds. Hence:

$$\frac{B}{C}+x_g=\frac{x_g^2}{1-2x_g}-\frac{1}{n-1}$$

or

$$\frac{B}{C}=\frac{x_g\,(3x_g-1)}{1-2x_g}-\frac{1}{n-1}.$$

If it were possible to express x_g as explicit function of n, it would directly appear, that k must be $> n$ to satisfy the circumstance that $\frac{dp}{dx} = 0$ shall pass through the top. Now we shall have to content ourselves with calculating the value of k for different values of n with the aid of the table (p. 829). Thus $\frac{1}{n-1} = 0{,}3704$ corresponds to $x_g = 0{,}4$, and we find $\frac{B}{C}$ then equal to $0{,}4 - 0{,}3704 = 0{,}0296$. As $\frac{B}{C} = \frac{1}{k-1}$, we find $k = 1 + \frac{1}{0{,}0296}$, n being $= 1 + \frac{1}{0{,}3704}$. Thus we find:

x_g	n	k
0,4	$1 + \frac{1}{0{,}37}$	$1 + \frac{1}{0{,}03}$
0,45	$1 + \frac{2}{3}$	$1 + \frac{1}{0{,}075}$
0,46	$1 + \frac{1}{2{,}08}$	$1 + \frac{1}{0{,}105}$
0,47	$1 + \frac{1}{3{,}06}$	$1 + \frac{1}{0{,}15}$
0,48	$1 + \frac{1}{5{,}04}$	$1 + \frac{1}{0{,}24}$
0,49	$1 + \frac{1}{10{,}91}$	$1 + \frac{1}{0{,}6}$.

So k always larger than n, but the ratio $\frac{k}{n}$ decreasing with n. That $\frac{B}{C} - \frac{1}{n-1}$ or $\frac{1}{k-1} - \frac{1}{n-1}$ must always be negative for the case that $\frac{dp}{dx} = 0$ passes through the top of $\frac{d^2\psi}{dx^2} = 0$, appears when we express the value of $\frac{B}{C} - \frac{1}{n-1}$ in x_g. This value is:

$$\frac{B}{C} - \frac{1}{n-1} = \frac{x_g(3x_g-1)}{1-2x_g} - \frac{2}{n-1}$$

or

$$\frac{B}{C} - \frac{1}{n-1} = \frac{x_g(1-x_g)}{1-2x_g} \left\{ -1 + \sqrt[3]{\frac{2(1-2x_g)^2}{x_g(1-x_g)}} \right\}.$$

The factor of $\frac{x_g(1-x_g)}{1-2x_g}$ is only $=0$ for $x_g=\frac{1}{3}$ and negative for every value of x_g between $\frac{1}{2}$ and $\frac{1}{3}$, between which values it lies.

For all values of $T < T_g$ the section of the two surfaces has the shape of fig. 24*a* (Contribution V, p. 134). For $T=T_g$, $\frac{d^2\psi}{dx^2}=0$ has contracted to a single point, and the line $\left(\frac{dp}{dx}\right)_{vT}=0$ has the minimum volume exactly at that point.

If we take k still larger than was calculated above the section of the two surfaces will pass round the top, and there is again question of a maximum temperature, which, of course, lies then again below T_g. At this maximum temperature there is again contact between the two curves, but then the contact is such that $\left(\frac{d^2\psi}{dx^2}\right)_{vT}=0$ lies entirely in the region where $\left(\frac{dp}{dx}\right)_{vT}$ is positive, except in the point of contact, where $\frac{dp}{dx}=0$. The point of contact lies then on the branch of $\left(\frac{dp}{dx}\right)_{vT}=0$, where $\frac{dv}{dx}$ is negative.

This, however, does not exhaust all possible cases for the intersection of the two surfaces. Some more remarks remain to be made. We first observe that if $\frac{da}{dx}$ is negative, there are no points of the intersection for the values of x for which this is the case. For such points $B+Cx$ is negative, which can only be the case for positive C if B is negative.

In the quadratic equation in $(v-b)$ the factor of $\frac{v-b}{\frac{db}{dx}}$ has become positive on account of $B+Cx$ being negative, and the third term is also positive, because $\frac{B-\frac{C}{n-1}}{B+Cx}$ has both its numerator and its denominator negative. So no positive value of $v-b$ can satisfy this equation. In the second place we observe that for the value of x for which $\frac{da}{dx}=0$, the value of $v-b$ is infinite, and the value of T

equal to 0. The projection of the section of the two surfaces on the v,x-plane is then a curve which starts at $x=1$ and $v=b_2$, and has an asymptote for the value of x for which $\frac{da}{dx}=0$. The T,x-projection of the section is then a line which has a value for T equal to zero at $x=1$ and $x=-\frac{B}{C}$, and which has a maximum T somewhere between these two values of x. It is clear that at this value of T, at which the curves $\left(\frac{d^2\psi}{dx^2}\right)_{vT}=0$ and $\left(\frac{dp}{dx}\right)_{vT}=0$ touch, the contact takes place as in the case discussed last, and that the top of $\frac{d^2\psi}{dx^2}=0$ lies in the region where $\frac{dp}{dx}$ is positive. And in the third place we draw attention to the special case that $B=0$, or $a_{12}=a_1$ or $k=\infty$. Then the value of x, for which $\frac{da}{dx}=0$, is itself equal to 0. The equation for the determination of $v-b$ of the section of the two surfaces simplifies then to:

$$\frac{(v-b)^2}{\left(\frac{db}{dx}\right)^2}-(1-x)\frac{v-b}{\frac{db}{dx}}-\frac{1-x}{n-1}=0$$

or

$$\frac{v-b}{\frac{db}{dx}}=\frac{1-x}{2}+\sqrt{\frac{(1-x)^2}{4}+\frac{1-x}{n-1}}$$

This represents a branch of a hyperbola which passes through the point $x=1$ and $v=b_2$ and cuts the axis $x=0$ for a value of:

$$v=b_1+\left(\frac{b_2-b_1}{2}\right)\left\{1+\sqrt{\left(1+\frac{4}{n-1}\right)}\right\}.$$

The quantity $k=\frac{a_2-a_{12}}{a_{12}-a_1}$, on which it depends in so high a degree whether the considered surfaces intersect or not, and the way in which they intersect, is, for the same value of a_2 and a_1, entirely determined by the value which we must assign to a_{12}. If a_{12} decreases from a_2 to a_1, k increases from 0 tot ∞. For $a_{12}=\sqrt{a_1a_2}$ it has the value $\sqrt{\frac{a_2}{a_1}}$ and then one of the transition cases $k=n$ would be $\frac{a_2}{n^2}=a_1$, or the critical pressure of the two components has the same value. But until the relation between a_1, a_2 and a_{12} is known, such a simple rule cannot be considered as valid.

The calculation of the temperatures at which the two curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{dp}{dx} = 0$ are in contact cannot be performed on account of the very intricate forms to which this problem leads. For this purpose we might solve the value of $v-b$ from the quadratic form of page 201, which is then a function of x, and substitute then the value of v, either in $\frac{dp}{dx} = 0$, or in $\frac{d^2\psi}{dx^2} = 0$. We have then a formula in which T is expressed in the values of x of the points of intersection of the two curves. If we seek the maximum value of T by differentiating with respect to x at $T =$ constant, we find a relation in x, from which the x of the points of contact would have to be calculated, and the value of T_{max} or T_{min} by substitution of this value of x. But even in the special case of $\frac{B}{C} = \frac{1}{n-1}$, or $k = n$, in which $v - b = \frac{db}{dx} \frac{x(1-x)}{\frac{1}{n-1}+x}$, this calculation leads to a form in which x rises to the third degree. In all other cases the equation is much more intricate. The value of x, v and T for the maximum and minimum temperature might of course also be calculated by the aid of the three eqations:

$$\frac{d^2\psi}{dx^2} = 0, \qquad \frac{dp}{dx} = 0 \quad \text{and} \quad -\frac{d^2\psi}{dx^2} \frac{d^2p}{dx\,dv} = \left(\frac{d^2p}{dx^2}\right)^2,$$

which last equation expresses that the two curves touch. As $\frac{d^2p}{dv\,dx}$ is certainly negative in the points of the line $\frac{dp}{dx} = 0$, $\frac{d^2\psi}{dx^2}$ must certainly be positive for the contact, which had already been represented in the figures 24 of these contributions.

Physics. — "*Anomalous refraction phenomena investigated with the Spectroheliograph.*" By Prof. W. H. Julius.

According to the current interpretation of spectroheliograph results, *dark* flocculi indicate regions on the sun, where the special gas, a line of which is used, exists in such conditions of density and temperature, that it strongly absorbs the light coming from deeper layers, whereas *bright* flocculi show us regions where, in consequence of higher temperature or chemical or electrical causes, the radiation of the gas exceeds its absorbing effect.

A few years ago I proposed an entirely different explanation of the same phenomena[1]). An attempt was made to account for the peculiar distribution of the light in photographs, secured with the spectroheliograph, by simply considering the anomalous refraction which waves from the vicinity of the absorption lines must suffer when passing through an absorbing medium, the density of which is not perfectly uniform.

If it proves possible to explain the observed facts on this basis, we shall be able to dispense with the assumption of any very marked differences as to the absorbing and emitting conditions of a certain gas or vapour in contiguous regions on the sun. Moreover, we then *might* assume the constituents of the solar atmosphere to be thoroughly mixed, their proportions in the mixture only varying with the distance from the sun's centre.

That our interpretation does not presuppose the separate existence of cloud-like masses of calcium or iron vapour or of hydrogen, simplifies the conception of the solar body, and therefore looks like an advantage; but even if one were compelled, by other considerations, still to believe in the real existence of such separate luminous or dark accumulations of certain substances, it would nevertheless be necessary to consider the effect, which anomalous dispersion of light in those masses must have on the appearances revealed by the spectroheliograph.

Among the advantages I derived from a visit to the Mount Wilson Solar Observatory, in August 1907, was the opportunity of using the 5 foot spectroheliograph[2]) for some experiments on anomalous refraction.

It was expected that when light, coming from a source with a continuous spectrum, traverses a space in which sodium vapour is unequally distributed, particulars concerning the distribution would be revealed by the spectroheliograph through the *refracting* power of the vapour, rather than through its absorbing and emitting power. This expectation could be put to the test.

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[1]) Proc. Roy. Acad. Amsterdam VII, p. 140, (1904).

[2]) Hale and Ellerman. "The five-foot spectroheliograph of the Solar Observatory." Contributions from the Solar Observatory Mount Wilson, California, N°. 7.

As an equipment for the study of anomalous dispersion phenomena in sodium vapour, exactly similar to the one described in my paper on "Arbitrary distribution of light in dispersion bands"[1]), had already been procured for the solar observatory by Professor HALE, the experiments were readily made, thanks to the laboratory facilities available on the mountain.

The apparatus consists of a wide nickel tube, 60 c.m. long, the middle part of which is placed in an electric furnace, while the projecting ends are cooled by jackets with flowing water. The tube contains a few grammes of sodium and is permanently connected to a Geryk-pump to remove the air and the gases which escape from the sodium during the first stages of the heating process. An arrangement is provided for, by which density gradients of various known directions and arbitrary magnitude may be produced in the sodium vapour.

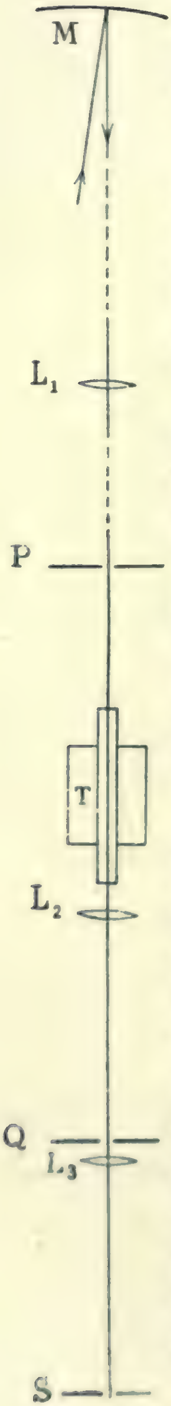

Fig. 1.

Sunlight coming from the 60 feet mirror M (fig. 1) of the Snow telescope[2]) passes through the tube T on its way to the slit S of the spectroheliograph. The distance between T and S is about 560 c.m. A lens L_1 gives an image of the sun near the middle of the tube T. P is a diaphragm with an adjustable slit, of which the lens L_2 projects an image in the plane of the diaphragm Q. Just behind the latter is a lens L_3; in combination with L_2 this forms an image of a section of the tube in the plane of the slit S of the spectroheliograph. In this image (fig. 2) the rectangular windows of the caps of the tube will of course come out with somewhat blurred edges, as only a section lying somewhere *between* the caps would show sharp. In A and B are projected the narrow nickel tubes[3]),

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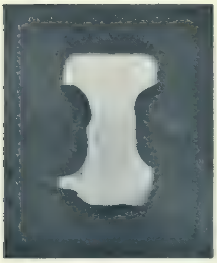
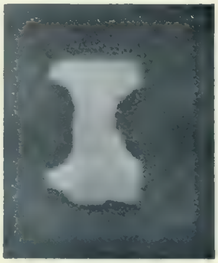
[1]) Proc. Roy Acad. Amsterdam, IX, p. 343. (1906).

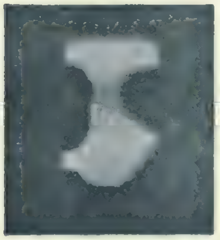
[2]) Described in: Contributions from the Solar Observatory Mt. Wilson, Cal., Nos. 2 and 4.

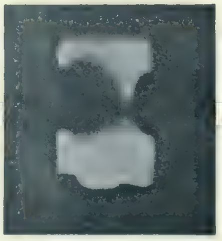
[3]) See description in: Proc. Roy. Acad. Amsterdam, IX, p. 345.

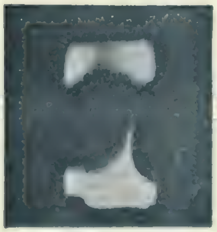
W. H. JULIUS. "Anomalous refraction phenomena investigated with the spectroheliograph."

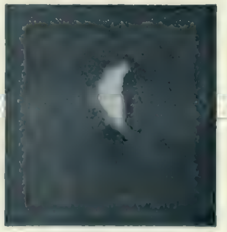
α


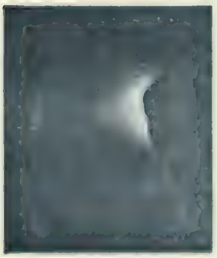
β


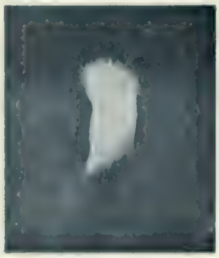
γ


δ


ε


ζ


η


θ


1

of which, for producing the required density gradients, the temperature may be varied at pleasure by forcing an electric current or an air current through them.

Cooling one of the tubes by an air current causes sodium vapour to condense on it; so, in course of time, drops of molten metal will hang from the tubes and fall off again.

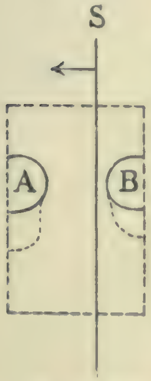


Fig. 2.

When a photograph is made, the first slit S of the spectroheliograph moves across the image in the direction of the arrow (fig. 2), and at the same time the second slit moves across the photographic plate.

Let us suppose the openings in P and Q (fig. 1) to be so adjusted, that the image of the slit in P exactly coincides with the slit in Q. Then all the light which passes through P and traverses the vapour along straight lines, is transmitted by Q and therefore contributes to the intensity of the image of the tube-section. Waves however that deviate so much in the sodium vapour as to be intercepted by the screen Q, will be absent from the spectrum of the transmitted light.

If the furnace is slowly heated to 380° or 390°, the density of the vapour is pretty uniform in the middle part of the wide tube and falls off towards the ends; but as the direction of these density gradients nearly coincides with that of the beam of sun-light, even the waves subject to anomalous dispersion will hardly deviate from the straight path. The D-lines in the spectroheliograph retain about their normal appearance. If now we blow air through the tube B, density gradients are produced all around it in directions perpendicular to the axis of that tube. The D-lines no longer show the same appearance throughout the field. In the spectrum of those parts of the field where perceptible gradients occur, the D-lines now appear winged; they are indeed enveloped in *dispersion bands*. As the width of these bands depends on the magnitude of the gradient, it will, in our case, vary along the lines and reach a maximum at the place in the spectrum which corresponds to the plane passing through the axes of the tubes A and B. And with increasing distance between S and B (fig. 2) the width of the bands will diminish.

Let us consider the monochromatic images of the tube-section produced by the spectroheliograph if the camera slit is set at different distances from the D-lines.

With the camera slit at λ 5850, outside the region of the dispersion band of D_2 the illumination of the field is uniform (see the Plate, *a*);

nothing is visible of the density gradients existing round the cooled tube B, because light of this wave-length travels along straight lines through the vapour.

Proceeding to $\lambda\,5870$, we are still at such a distance from D_2, that the value of $\frac{1-n}{\Delta} = R$ (n representing the index of refraction, Δ the density of the vapour) is moderate. Steep gradients of the density are required to make the rays deviate sufficiently for missing the slit in Q, and such gradients are only to be found very near the surface of the tube B. We therefore obtain the image β, in which B appears surrounded by a narrow dark region.

The third photograph, γ, has been made with $\lambda\,5877$. For these waves the expression $\frac{1-n}{\Delta}$ is greater than for $\lambda\,5870$, so that smaller values of the gradient suffice to give to the rays a perceptible incurvation. The result is a broader dark region all round B ¹).

The photographs δ and ε have been secured with the camera slit on $\lambda\,5881$ and $\lambda\,5885$ respectively. This time the tube A has been cooled instead of B. We see the dark "aureole" grow as the wave-length we are using approaches $\lambda_{D_2} = 5890$. Getting nearer still, the whole field would finally become dark.

Similar results are obtained if we approach D_1 from the side of the *greater* wave-lengths, thus using waves for which $\frac{n-1}{\Delta}$ has increasing values.

By a slight change in the arrangement of our experiment we may obtain the opposite effect, to wit, that merely rays, suffering anomalous refraction, do enter the spectroheliograph, whereas the normally refracted light is prevented from reaching the slit. We have only to open the slit in P very wide, and to put a vertical bar (a match for instance) in the middle of it, the image of which now falls exactly on the slit in Q. Under these circumstances light, issuing from the divided opening in P, can only be transmitted by Q if it has been deflected in the vapour.

In this way the photographs ζ, η and θ were obtained, the second slit being set on $\lambda\,5884$, $\lambda\,5886$, $\lambda\,5888$ respectively. If there had been no density gradients, the whole field would have shown dark; the *bright* regions, however, now prove the existence of the gradients. When taking ζ and η, the tube B, and when taking θ, the tube A was cooled.

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¹) In this image the lower right corner was cut off by a rubber tube accidentally crossing the path of the beam.

The following general statement is borne out by these experiments. If an illuminated absorbing vapour is investigated by means of the spectroheliograph, and the camera-slit of the instrument is set *on the edge* of a dispersion band, marked irregularities in the brightness of the field will only appear at those places in the image which correspond to regions with *large* density gradients in the vapour. Setting the slit *nearer to the middle* of the dispersion band, we shall get evidence, in the image, also of regions with *smaller* gradients, a.s.o. Particulars regarding the distribution of a vapour are thus clearly shown by the spectroheliograph through anomalous refraction, even in cases, where the absorbing or emitting power of that medium would have failed to reveal its structure.

The bearing of these inferences on astrophysical phenomena has now to be considered a little more closely.

Suppose we have a large mass of absorbing vapour of such average density, that, if it were uniform, its absorption lines would appear rather narrow; and of such temperature and condition of luminescence that its emission lines are very faint. As soon as the density of this mass becomes irregular, some parts of it may give rise, when traversed by light from another source, to the appearance of dark or bright dispersion bands, greatly exceeding in width and strength its absorption or emission lines.

It is therefore *possible*, that anomalous refraction plays a very essential part in the production of those phenomena which the student of astrophysics observes with his spectroscope or spectroheliograph; we must inquire how far this is also *probable*.

One might be inclined to object, for instance, that in our experiment the use of a narrow and sharply limited source of light, placed at a fair distance behind the vapour, seemed to be a necessary condition for obtaining any marked dispersion effects, and that in the sun similar circumstances are very unlikely to prevail. Indeed, the bulk of the sun — whatever the nature of the photosphere may be — is a large incandescent mass, closely surrounded by the absorbing vapours, so that the "source of light", if considered from a point of the chromosphere, subtends a solid angle of nearly 2π. The reversing layer and the chromosphere have sometimes been compared to a thin, transparent layer of selectively absorbing varnish, covering a luminous (e.g. phosphorescent) globe: the photosphere. It seems very improbable that refraction in density gradients of such a transparent envelope should be able to disturb to any perceptible degree the uniform brightness of that globe.

The comparison, however, is entirely misleading, because, so far, an essential relation between absolute size and density gradients is overlooked in it. But if carried through properly, it will lead us to the opposite conclusion, namely that refraction in the solar atmosphere must alter the distribution of the light on the disk entirely.

If we wish to form an image, on a reduced scale, of the sun considered as a refracting body, we have to reduce the radii of curvature of the rays in the same proportion as we do the diameter, for instance 10^{10} times (so as to make the diameter of the photosphere 14 cm.). By the general equation [1])

$$\frac{d\Delta}{ds} = \frac{1}{R\varrho} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

we know that, for a given value of the refraction constant R, the radius of curvature ϱ of a beam of light is in reverse proportion to the density gradient $\frac{d\Delta}{ds}$ in the direction toward the centre of curvature. In our image, therefore, the density gradients have to be taken 10^{10} times as great as they are in the sun.

Let us suppose that at a certain level in the solar atmosphere irregular density gradients occur, which are of the same order of magnitude as the radial (vertical) density gradient in our earth's atmosphere, viz. 16×10^{10} [2]). At the corresponding points in our image we then have to put $\frac{d\Delta}{ds} = 16$. If the layer of "varnish" were really traversed by many density gradients of this order of magnitude, it would be very different from ordinary transparent varnish, and certainly be able to disturb the uniform brightness of the background, like a layer of glass beads or swollen sago grains. Even normally refracted waves would perceptibly deviate in an envelope of this kind. For if in our equation (1) we put $\frac{n-1}{\Delta} = R = 0{,}5$ and $\frac{d\Delta}{ds} = 16$, we get $\varrho = 0.125$ cm., so that the average curvature of such rays is already sufficient for producing sensible changes in the divergence of beams on their way through a shell not thicker than 0.1 cm

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[1]) Proc. Roy. Acad. Amsterdam, IX, p. 852. (1906).

[2]) The frequent occurrence of density gradients nearly perpendicular to the radii of the sun is rendered more probable still, since increasing evidence has been obtained by Prof. HALE of the existence of solar vortices, in which the convection currents (especially in sun-spots) are sufficiently strong to produce magnetic splitting of absorption lines. (Cf. Nature, Vol. 78, p. 368—370, Aug. 1908).

Waves, suffering anomalous refraction, will of course be much more scattered by the same medium. Let us consider an absorbing substance which, at a certain level, occupies say only 1 percent of the solar atmosphere, taken as a perfect mixture. Its density gradients will then be only $\frac{1}{100}$ of those of the mixture. The refraction constant, on the other hand, for waves near one of its absorption lines, may attain values as high as 1000 or 2000. With $R = 1600$ (as actually observed in sodium vapour, Proc. Roy. Acad. Amst. IX, p. 353), our equation (1) becomes

$$\frac{1}{100}\frac{d\Delta}{ds} = \frac{1}{1600\,\varrho}.$$

In a level where, in our image, the irregular density gradients of the envelope were supposed to have an average value $\frac{d\Delta}{ds} = 16$, the equation gives

$$\varrho = 0{,}004 \text{ cm}.$$

It is evident that under such circumstances rays may easily deviate 90 degrees and more in the thin shell of transparent matter covering our globe, and thus give rise to a very unequal distribution of the light in photographs of it, secured with the spectroheliograph.

This conclusion holds just as well with regard to the real sun. It follows directly from our *only* assumption, that in some level of the sun irregular density gradients exist, comparable in magnitude with the vertical gradient in the earth's atmosphere. At lower levels, greater gradients, at higher levels, smaller gradients may be expected to prevail. As the validity of this assumption can hardly be doubted, we may infer that the existence of some important influence of anomalous dispersion on astrophysical phenomena is not merely possible, but *exceedingly probable*, in spite of the absence of narrow slits as sources of light.

Although we are free to admit that the phenomena, observed with the spectroheliograph on the solar disk, are perhaps in part due to selective radiation, dependent on various conditions of temperature or luminescence, we may nevertheless inquire into some consequences to which one is led if only the effects of refraction in a mixture of vapours are considered.

The composition of the solar atmosphere cannot be the same at all levels. As we get lower down, the percentage of heavier molecules is likely to increase; but we should not presume too much as to the order in which the elements will come into evidence, on account of possible condensation, and because the pressure of radiation counteracts gravitation to a degree that depends on the size of the particles, and, therefore, on numerous unknown conditions prevailing in the sun.

Yet for each element a certain level must exist, in which its percentage in the mixture is a maximum. Accordingly, the refracting properties of successive layers will be governed by different elements. A photograph, made with the spectroheliograph in a hydrogen line, shows a structure which, of course, depends on the distribution of all the hydrogen present in successive layers, but is chiefly determined by the density gradients in a rather high level; whereas a photograph, made with an equally strong iron-line, reveals more especially the structure of lower regions. This explains the difference in character between iron- and hydrogen plates.

It must be possible, on the other hand, to obtain almost identical photographs with different lines, provided they belong either to the same element, or to elements that are most in evidence at about the same level in the sun; but then another condition has also to be fulfilled, viz. that the camera-slit transmits rays of the same refrangibility in both cases. If for instance Fig. 3 represents the dispersion curve near H_α and near H_δ, the width and the position of the camera-slit ought to be so chosen, as to let in only waves corresponding to parts of the curve, enclosed between equal ordinates in the two dispersion bands [1]).

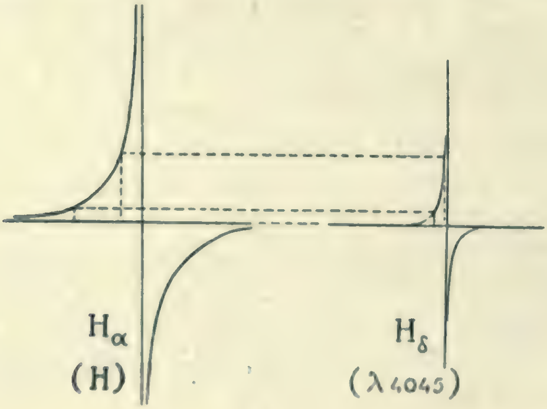

Fig. 3.

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[1]) Waves, lying more or less symmetrically on either side of an absorption line, and answering the relation $n-1 = 1-n'$ between the indices of refraction n and n' of the medium for them, must give nearly the same spectroheliograph results on the greater part of the disk. This follows from a discussion of the various possi-

Recently it has been found by Prof. **Hale** that, while the H_β-, H_γ- and H_δ-lines give very similar results, photographs with the much stronger line H_α are widely different in some respects 1)). Bright flocculi appear on these plates at points where no corresponding objects are shown by H_δ. Moreover, the dark H_α-flocculi, while showing a general agreement in position and form with those of H_δ, are stronger and more extensive. In some instances, however, small areas appear dark in H_δ which are absent or fainter in H_α.

Such differences are of the same character as those observed between photographs made with the slit in the broad calcium-bands H or K at various distances from the central line. They may find a corresponding explanation if we assume that the rays, used in the H_α photographs, were on the average refracted to a higher degree than those, used in the H_δ-photographs, but both by the same system of density gradients. It is not improbable, therefore, that in the wings of H_α waves may be selected so as to give spectroheliograph results, closely resembling H_δ-plates.

That also lines of *different* elements may give very similar results with the spectroheliograph, is exemplified by the case of calcium and iron. Among the beautiful collection of photographs secured on Mount Wilson I saw several iron-(λ 4045)-plates rather closely resembling certain calcium-(H_1)-plates of the same daily series. As the atomic weights of calcium and iron are not so very different, and their levels of maximum density therefore probably not far apart, the refraction caused by these elements may bring out the density gradients of nearly the same layer of the solar atmosphere. It will do so by showing a similar distribution of the light in the two photographs — provided that rays of the same refrangibility are used in both cases. And this condition may be fulfilled by setting the camera slit on corresponding regions of the spectrum, in the sense as illustrated by Fig. 3, if we imagine it now to bear on the calcium-(H)-line and the iron-(λ 4045)-line.

With a calcium- and a hydrogen-line such similarity could not be found.

Far more evidence will of course be required before we shall be able to decide whether or not anomalous dispersion is the principal agent in determining the flocculent appearance of the solar disk.

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bilities regarding the relative position of density gradients and source of light. Consequently a H_δ-plate, obtained with the camera-slit centrally, so as to embrace the whole width of that rather narrow dispersion band, will scarcely differ, at first sight, from a photograph made with only one of the wings.

2)) **Hale**, "Solar vortices", Contrib. from the Mt. Wilson Solar Obs. No. 26.

Plates secured with many lines of various elements will have to be compared. The mighty 30-foot spectroheliograph of the "tower telescope" of Mount Wilson is excellently adapted to work of this kind, not only on account of its great dispersion permitting the use of finer lines, but chiefly because it is provided with two camera slits, so that perfectly simultaneous photographs with different lines may be secured. By this arrangement, really comparable monochromatic pictures of the sun are obtained, since the otherwise confusing influence of the variable refraction in our atmosphere is thus rendered harmless.

I feel greatly obliged to Prof. GEORGE E. HALE for having procured for me the opportunity of making an investigation at the Mount Wilson Solar Observatory, but more still for his keen and stimulating interest in the problems, suggested by the application of the principle of anomalous refraction in astrophysics. I am also very much indebted to the kindness of Mr. F. ELLERMAN, Mr. W. S. ADAMS and Dr. CH. M. OLMSTED for valuable information and assistance in connection with the inquiry here reported upon.

Physics. — "*The* ZEEMAN-*Effect of the strong lines of the violet spark spectrum of iron in the region* λ 2380—λ 4416." By Mrs. H. B. VAN BILDERBEEK-VAN MEURS. (Communicated by Prof. P. ZEEMAN).

The concave ROWLAND grating used in the experiments here communicated has 14438 lines per inch, a width of 8 c.m., and a radius of curvature of 304.96 c.m. The grating is mounted according to RUNGE and PASCHEN's method.

The spark passed between the iron poles of the magnet in the direction of the line of force. It was originated by the discharge of the secondary coil of a RUHMKORFF, a self-induction and condenser being placed in parallel.

Further details will be given in my thesis for the doctorate.

The time of exposure varies from 30 to 120 minutes.

In order to determine the field strength I made simultaneous exposures of the iron and zinc spectra. The amount of separation of the zinc line 4680.33 was compared with the result of the measurements of COTTON and WEISS (Journal de Physique, June 1908), the strength of field being supposed proportional to the amount of separation.

λ	I	$\delta\lambda$ vibr. ⊥ field	$\delta\lambda$ vibr. / field	$\frac{\delta\lambda}{H\lambda^2}\,10^{13}$ vibr. ⊥ field	$\frac{\delta\lambda}{H\lambda^2}\,10^{13}$ vibr. // field
2382.17	10	0.214		11.80	
2395.74	4	0.206		11.23	
2562.65	5	0.238		11.34	
2585.98	10	0.292		13.66	
2598.46	8	0.310		14.36	
2599.50	20	0.334		15.46	
2607.17	10	0.315		14.50	
2611.99	10	0.335		15.36	
2617.70	6	0.361		16.48	
2625.70	4	0.324		14.70	
2628.39	8	0.229		10.37	
2631.12	4	0.299		13.51	
2631.44	3	0.289		13.06	
2727.64	6	0.379		15.94	
2739.63	15	0.327		13.63	
2743.28	8	prob. unaffected			
2746.60	10	0.222		9.206	
2747.08	8	0.306		12.69	
2749.41	20	0.272		11.26	
2753.40	5	0.245		10.11	
2755.80	15	0.278		11.45	
2767.60	5	0.418		17.07	
2967.03	5	0.320		11.37	
2994.58	3	0.439		15.31	
3001.09	2	0.397		13.79	
3002.82	3	0.388		13.45	
3008.26	2	0.413		14.28	
3020.80	3	0.412		14.13	
3037.51	3	0.433		14.68	
3047.72	3	0.440		14.82	
3057.57	3	0.345		11.54	
3059.20	3	0.446		14.91	
3227.91	5	0.354		10.63	
3440.79	4	0.434		11.47	
3466.01	3	0.759	0.389	19.77	10.13
3475.60	3	0.625	probably div.	16.19	
3490.76	4	0.574	" "	14.74	
3497.99	3	0.772		19.74	
3513.98	3	0.555		14.06	
3555.08	4	0.516		12.77	
3558.69	4	diffuse			
3565.53	5	0.349		8.589	
3570.29	10	0.420		10.31	
3581.34	10	0.460		11.22	
3585.48	3	0 446	0.387	10.85	9.418
3587.11	3	diffuse	0.489		11.89
3606.85	4	0.429		10.32	
3609.01	6	0.183		4.395	
3618.91	6	0.327		7.811	
3631.62	6	0.368		8.729	
3647.99	6	0.391		9.192	
3649.62	3	0.493		11.58	
3680.09	3	0.574	probably div.	13.26	
3687.61	4	0.626		14.40	
3705.72	4	0.565	0.262	12.87	5.969
3709.40	4	0.632		14.37	
3720.09	10	0.496		11.21	

λ	I	$\delta\lambda$ vibr. $\perp$ field	$\delta\lambda$ vibr. // field	$\frac{\delta\lambda}{H\lambda^2}\ 10^{13}$ vibr. $\perp$ field	$\frac{\delta\lambda}{H\lambda^2}\ 10^{13}$ vibr. // field
3722.71	4	0.558	0.392	12.60	8.849
3727.78	5	0.659		14.84	
3733.47	3	0.355 0.354	0.587	7.968 7.945	13.17
3735.00	10	0.592		13.28	
3737.28	7	0.459		10.28	
3745.70	5	0.474		10.57	
3748.40	4	0.276	perhaps divided	6.145	
3749.62	10	0.574		12.77	
3758.39	8	0.540		11.96	
3763.98	6	0.422		9.318	
3765.70	3	0.484		10.68	
3767.36	5	0	0	0	0
3795.14	5	0.692		15.03	
3799.70	5	0.662		14.34	
3805.48	3	0.386		8.339	
3813.12	4	0.414		8.908	
3816.00	10	0.495		10.63	
3820.61	10	0.529		11.34	
3821.57	5	0.694		14.84	
3826.08	8	0.494		10.56	
3828.00	7	0.451		9.629	
3834.41	6	0.431		9.170	
3840.61	4	0.303		6.426	
3850.19	4	0	0	0	0
3856.55	5	0.690		14.51	
3860.12	6	0.682		14.32	
3865.75	4	0.348 0.348	0.658	7.285 7.285	13.78
3872.70	4	0.594	0.473	12.39	9.866
3878.20	4	0.812		16.89	
3878.78	5	0.715		14.87	
3886.45	5	0.802		16.61	
3895.80	3	0.676		13.93	
3903.10	5	0.544	0.217	11.17	4.456
3920.41	4	0.634		12.90	
3923.08	4	0.694		14.11	
3928.09	4	0.705		14.29	
3930.47	4	0.715		14.48	
3969.43	5	0.758		15.05	
4005.41	6	0.787		15.35	
4045.99	15	0.618		11.81	
4063.78	10	0.544		10.31	
4071.90	8	0.351		6.623	
4181.92	4	0.700		12.52	
4199.27	5	0.577		10.24	
4202.21	6	0.617		10.93	
4236.12	4	0.982		17.12	
4250.19	6	0.537	0.404	9.266	6.994
4260.70	10	0.878		15.13	
4271.99	10	0.705		12.09	
4294.32	4	0.698		13.21	
4299.43	4	0.790		13.37	
4308.10	15	0.648		10.92	
4325.97	15	0.528		8.826	
4383.73	20	0.697		11.35	
4404.95	15	0.678		10.93	
4415.30	10	0.654		10.50	

The strengths of field used in all other exposures, could be determined by comparison of corresponding iron lines in the spectrum under review and in the standard iron-zinc spectrum.

The field strengths utilised were near 30000 Gauss. In the following table all separations are reduced to $H = 31965$ Gauss.

A calcite rhomb introduced between the spark and the focussing lens made it easy to get separate exposures of vibrations perpendicular to resp. parallel to the field. The plates used were Dr. SCHLEUSSNER's Spezial Rapid plates. They were developed with Edinol.

In the following table $d\lambda$ and λ are given in Å.U. The wavelengths and intensities are taken from EXNER and HASCHEK's tables.

In the case of triplets and quartets $d\lambda$ indicates the difference of the wavelengths of the two outer components vibrating perpendicular or parallel to the lines of force. In the case of quintets for vibrations perpendicular to the lines of force the difference of wavelengths of the components towards red and violet to the central one are given. For vibrations parallel to the lines of force the data are given as in the case of triplets.

Probably some triplets can be subdivided further, but even an approximate knowledge of the magnetic separation of the iron lines has become recently of some value by HALE's important discovery concerning the spectrum of sun-spots[1]).

I hope to give in my thesis references to the literature of the subject.

Anatomy. — "*The nervous system of a white cat, deaf from its birth: A contribution to the knowledge of the secondary systems of the auditory nerve-fibres*". By Prof. C. WINKLER.

Through the kindness of Prof. ZWAARDEMAKER, speaker got in his possession the nervous system of a white blue-eyed cat, which during life, though most carefully observed, never reacted on acoustic stimuli, consequently deaf from its birth[2]).

This nervous system had been slightly damaged in the removing,

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[1]) GEORGE E. HALE. Solar Vortices and the ZEEMAN-Effect.

P. ZEEMAN. Solar Magnetic Fields and Spectrum Analysis. Nature. Vol. 78, p. 368 and 369, 1908.

[2]) Prof. ZWAARDEMAKER writes on this subject the following:

"This white catt, born of a white mother with normal hearing (one albino-eye) "was obviously deaf from its birth. At any rate it was kept under observation "since birth, and never a single reaction on acoustic stimuli was obtained. Even probably because the tentorium, ossified in these animals, had been drawn through the occipital pole of the hemispheres.

With the exception of this damaged portion it was possible to make a continuate series of frontal sections, partly after the WEIGERT-PAL method, partly coloured by means of carmine, which could be compared with the existing series of frontal sections from brains of normal cats.

The first thing noticed was that the peripherical octavus-roots which were attached to the oblongata, although smaller than in the compared preparations, *had not suffered any change*. In accord with this fact no degenerations were found either in the lateral rootfibres upon the corpus restiforme, or in the rootfibres in the ventral nucleus of the VIIIth nerve, or in the deep medullated layers of the tuberculum acusticum (speaker exhibits the microphotograms demonstrating those rootfibres.)

Although these nuclei too are somewhat smaller than in the compared series, yet it is impossible *that the deafness of this cat should have been occasioned by a primary affection of the labyrinth*. For in that case the well-determined and distinctly confined atrophies would have been found in the systems of primary rootfibres, which are in all cases consequent to the removal of the labyrinth in newborn animals. (These atrophies are demonstrated by the speaker on preparations and microphotograms of brainsections taken from rabbits where the labyrinth had been removed shortly after birth).

Those atrophies however were not found in the brain of this cat. The more striking is the fact that a secondary system of fibres, the dorsal octavus-tract, the so-called stria acustica (v. MONAKOW)

“an express investigation with the continuate note-series and with strong sound-“stimuli gave only negative results.

“The statical organ on the contrary was proved to be perfectly normal. On “the 7th of June 1908, shortly before death, this was carefully studied in my “Laboratory.

“Climbing along the frame of a rotation-apparatus was done in the normal “manner, likewise leaping from a chair. During rotation, when shut up in a “blackened chest, with an aperture on the upperside in order to facilitate the “observing of what is going on within, nystagmus of the head and of the eyes “was shown in the usual way.

“On stopping the apparatus, a typical instance was observed of the well-known “after-rotation, described once again by Mr. VAN ROSSEM (Sensations and reflexes, “having their origin in the semi circular canals Diss. 1907, Utrecht).

“Upon the small experimentation-lift of W. MULDER, whilst seeing is excluded, “all otolittic reflexes are recognized, and nowise impaired.

“During life the animal mewed.”

in the deaf-born cat does not attain to $^1/_4$ of the compass that fascicle presents in the series taken for comparison.

The fibres originating in this fascicle and decussating in the raphe (the vigorous decussation of von Monakow) are nearly all wanting. Monakow's decussation is represented barely by a few small fibres.

Likewise the fibres of **Held** and their decussation are almost entirely wanting. On the other hand, the ventral secondary octavus-tract in the ventral layers of the corpus trapezoides is represented by a vigorous layer of fibres decussating in the raphe.

Together with the loss of Monakow's decussation the area at the dorsal and frontal top of the superior olivary bodies, where the fibres of Monakow's and Held's crossings meet, is only represented by a few transverse sectioned fibres. It is wanting, and this deficiency in its turn is accompanied by a very important atrophy of the lateral lemniscus, more especially of its medial bundle of fibres. (The preparations and microphotograms illustrating this, are exhibited by the speaker).

Apparently nature did achieve in this cat, by some morbid process, a similar experiment as was made long ago by von Monakow[1]), when he was the first who succeeded in isolating the dorsal octavus-tract by sectioning the lateral lemniscus.

For if the lateral lemniscus is sectioned, this so-called Monakow's decussation atrophies rather completely and the stria acustica is reduced to a small rest, whilst the large cells in the opposite tuberculum acusticum have nearly all disappeared and a certain number of cells are atrophied as well in the nucleus ventralis as in the portio interna corporis restiformis and in the nucleus of Deiters. (The experimental loss and atrophy of those cells is demonstrated by means of preparations and microphotograms of brain-sections taken from rabbits, on which the section of the lemniscus had been performed directly after birth).

In the deaf-born cat almost all the large cells in the tuberculum acusticum have disappeared on both sides (and here — not in the loss of fibres — lies the cause of the slight decrease of the primary nuclei) whilst those in the dorsal portion of the nucleus ventralis, in the portio interna of the corpus restiforme and in the nucleus of **Deiters** are partly atrophied.

This case therefore supplies a new argument in favour of the opinion *that the secondary system of true auditory nerve-fibres are to be sought for in the dorsal and intermediate octavus-tracts, in the*

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[1]) C. von Monakow. Striae acusticae und untere Schleife. Archiv für Psychiatrie. 1891. Bd. XXII. S. 1.

decussations of MONAKOW *and* HELD, *and not in the ventral layers of the corpus trapezoides.*

This opinion, put forward long ago by VON MONAKOW [1]) in opposition to the now generally accepted opinion of the school of FLECHSIG which presumes the course of the auditory fibres to be lying in the ventral systems of the corpus trapezoides, has been upheld by the speaker also once before. [2])

The preparations from the deaf-born cat moreover enable us to find an answer to the question how this remarkable degeneration may be occasioned by a pathological process.

As is well-known, the roof of the 4th ventricle expands laterally into a so-called recessus lateralis, by which passes the tela chorioidea and consequently this latter is lying free at the ventral border of the oblongata.

At the entrance of this recessus, medial from the tuberculum acusticum (which forms the medial boundary of the recessus), the stria acustica is situated directly under the ependyme of the ventricle free at the surface.

Each hydrops ventriculi, tending towards dilatation of the recessus lateralis, becomes a danger for its surroundings, which may be oppressed either from the recessus lateralis as from the ventricle. It threatens to destroy successively first the stria acustica, next the tuberculum acusticum, and only after this latter the lateral root fibres become exposed. Now hydrops ventriculi may be caused by many different morbid processes, both of meningitis, ascending along the tela, and of encephalitis, complicated with ependymitis.

Now in this deaf-born cat we find hydrops ventriculi with a very important distention of the recessus lateralis, the tela chorioidea is thickened, with neo-formation of bloodvessels. The distention of the ventricle and that of its recessus undermined the lateral wall of the oblongata and the stria was pinched off (This distention is demonstrated by the speaker on preparations and microphotograms).

Similar dilatations of the recessus with the tumefaction of the tela accompanying them, were found also in the IVth ventricle of deaf-and-dumb persons, together with atrophy of the stria acustica. The lateral root-fibres however were not always intact in such cases. They were sometimes destroyed, sometimes not. These facts will soon be published by Mr. A. BROUWER in his dissertation.

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[1]) MONAKOW, l. c.

[2]) C. WINKLER. The central course of the N. Octavus. Proceedings of the Royal Acad. of Sciences, 1907.

In our deafborn cat the hydrops ventriculi is nevertheless secondary to a morbid process situated elsewhere.

For in the left hemisphere are found the residua of a process of encephalitis having occurred long ago, in casu before birth.

This focus is situated in the left corona radiata and in the radiation of the corpus callosum. The cortex remains uninjured. Loss of fibres, tumefaction of glia-elements, formation of cavities and neo-formation of vessels mark the place where the focus is found.

Frontalward its boundary nearly coincides with the place where the gyrus lateralis divides into a gyrus ecto- and ento-lateralis. Thence it expands below the gyri supra- and ecto-sylvii mediales, caudalward not passing beyond the fissura ecto-sylvia posterior. There is a secondary atrophy of the medullated radiations of the following convolutions: the gyrus splenialis, supra-splenialis, ecto-lateralis, supra-sylvius medialis and ecto-sylvius medialis and in the lateral portion of the gyrus ecto-sylvius posterior. (Speaker demonstrates the position of this focus with the aid of drawings, preparations and micro-photograms).

This morbid process has entailed consequences.

1. The hydrocephalus internus mentioned before, which has distended the lateral ventricles, the third ventricle, the aquaeductus and the fourth ventricle, in the latter mere especially the recessus lateralis.

2. The macroscopically visible atrophy of the radiations towards the aforesaid convolutions and in the fibres of the corpus callosum.

3. The atrophy of cells, more intensive in the before-mentioned convolutions, though also very evident in other convolutions of the left hemisphere and likewise in the right hemisphere.

A loss of cells does not exist in the anterior convolutions, it begins far behind the zone where the pyramides of Betz are found. The posterior pole was too much damaged to allow of any examination. But in the medial portions of the brain the degeneration is the following:

The loss and atrophy of cells is localized in the medial layers of cells of the cortex. The first layer of granular cells and that of the small pyramides are only slightly damaged, but the 4th stratum or interior granular layer and the 5th so-called sub-granular layer of the pyramides have lost all or a great number of the cells, the 6th or polymorphous layer of cells being again intact.

4. A macroscopically visible atrophy of the ventral nucleus of the left thalamus opticus, which has almost entirely disappeared at its frontal end and has lost cells as well as fibres.

5. A very slight atrophy in the most caudal part of the left

corpus geniculatum mediale, the more remarkable because therein many cells are lost, only there, were the bracchium conjunctivum from the ganglion quadrigeminum posticum enters in the corpus mediale. At the same time the atrophy in the left bracchium conjunctivum is more important than that on the right side. The preponderance of the atrophy in the left bracchium, in accordance with the atrophy of the lateral lemniscus described before, is considered by the speaker as being occasioned by the encephalitic process. This focus was not situated (or only to a very small extent) in the temporal radiation of the corona radiata. It is not followed by an intense atrophy in the homolateral corpus geniculatum mediale, and therefore, cannot in itself be held answerable for the auditory defect of the animal.

This deaf-born white cat with the blue eyes consequently may not be considered to be a deaf variety of the genus cat. It is a pathological product. An encephalitis, probably during the intra-uterine life, has destroyed a part of the left hemisphere (not the so-called auditory radiation) and occasioned a hydrocephalus internus. Its pression became a danger to all the systems at the surface of the ventricles. More especially those systems were endangered that were threatened from both sides by compression according to their position on the border of the recessus lateralis. The stria acustica was destroyed in that way.

Botany. — "*On the investigations of* Mr. A. H. Blaauw *on the relation between the intensity of light and the length of illumination in the phototropic curvatures in seedlings of Avena sativa.*" By Prof. F. A. F. C. Went.

Some years ago Wiesner[1]) attempted to ascertain, what is the minimum intensity of light to which various plants still react phototropically. He found, for instance, that with the epicotyl of *Pisum sativum* and the hypocotyl of *Lepidium sativum* the limit of sensitiveness is not yet reached at 0.054 normal candle power. (Wiesner expresses it in a unit which is equal to 6.5 Spermaceti candles). For the epicotyl of *Phaseolus multiflorus* the limit is exactly at 0.054 normal candle power. While in this case, the author does not mention the duration of the experiments, he states for the epicotyl of

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[1]) J. Wiesner. Die heliotropischen Erscheinungen im Pflanzenreiche. Wien 1878. p. 178—180.

Vicia sativa, that, at an intensity of 0.054 N.C., the curvature began to appear after 3 hours and 45 minutes, whereas the same organ in *Vicia Faba*, with light of the same strength, did not show any curvature even after 48 hours. In none of these cases, therefore, has an attempt been made to find the minimum period, during which light of a given intensity must act on a plant in order to produce a phototropic curvature. Later FIGDOR [1]) carried out similar experiments; here only his conclusion can be mentioned, that the inferior limit of phototropic sensitiveness is below 0.0003262 normal candle power for seedlings of *Lepidium sativum*, *Amarantus melancholicus ruber*, *Papaver paeoniflorum* and *Lunaria biennis*.

CZAPEK [2]) on the other hand has been engaged on a determination of the presentation-time; by this he means the minimum period of unilateral illumination, required for the subsequent production of a phototropic curvature. For seedlings of *Phalaris* and of *Avena* this period is stated by him to be about 7 minutes, although he furnishes no data as to the intensity of the light employed. Presumably the author did not perceive the necessity of such data, because his investigation was almost wholly concerned with geotropism, where the idea of presentation-time, without further specification, has a pretty definite meaning, because we are concerned with the constant force of gravity.

The question, whether there is a connexion between this presentation-time and the intensity of the light, was however close at hand. In his further investigation, on the perception of phototropic stimuli, Mr. A. H. BLAAUW has also taken up this question in my laboratory; he has arrived at some very striking results, about which I wish to make this brief preliminary communication.

The experiments were performed with etiolated seedlings of *Avena sativa*, the coleoptile of which is extremely sensitive to light stimuli, as is well known since the investigations of DARWIN and of ROTHERT.

For the weaker intensities an Auer von Welsbach burner (incandescent gas light) was used; it was kept very constant by means of a gas-pressure regulator. By placing the objects at varying distances from the lamp, and, where necessary, by screening the light through smoked glass, and further, by letting the light fall on a plate of opalescent glass with a diaphragm, which in its turn acted as source of light, all possible intensities were obtainable, from 100 Hefner candles downwards. The intensity was measured by means of a **Weber** photometer. The gaslamp was outside the room containing the experimental plants, so that the latter were protected against any harmful effect of coal-gas.

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[1]) W. FIGDOR. Versuche über heliotropische Empfindlichkeit der Pflanzen. Sitz ber. d. Math Naturw. Classe d. K. Akademie der Wissensch Wien. Bd. CII. Abth. I 1893, p. 45.

[2]) F. CZAPEK. Weitere Beiträge zur Kenntniss der geotropischen Reizbewegungen. Jahrbücher für wissenschaftliche Botanik. Bd. XXXII. 1898. p. 185.

For greater light intensities the electric arc-lamp of a lecture lantern was used, and by concentrating its light through lenses, strengths up to 48000 Hefner candles were obtainable.

The period of illumination varied from 13 hours to 0.001 second; the very short periods were obtained by means of a photographic instantaneous shutter with slit.

The plants were now placed at various distances from the source of light; they were illuminated for a given time and were then left in the dark and were examined for phototropic curvature after about 2 hours. When the distance and time had been properly chosen, a well-marked limit was found to occur, so that below a certain strength of light no curvature occurred, whereas above that strength all or nearly all the seedlings were bent towards the light. It may be said, therefore, that with a given exposure-time, a certain minimum intensity of light is required for perception, or, more correctly, for the production of a reaction, since of the actual perception of a light stimulus we know nothing.

It was already a striking result, that while, as stated above, the presentation time was assumed to be 7 minutes, Mr. **Blaauw** in his experiments still obtained a reaction when the exposure was diminished to 0.001 second, provided the light was very strong.

The results become still more important if expressed numerically, as in the following table. The first column gives the length of the exposure, the second the corresponding intensity of the light (in Hefner candles) which just sufficed for a phototropic reaction; the third column gives the product of these two magnitudes, the time being expressed in seconds, so that the product might be called candles-seconds. In other words, the third column indicates in every case, how much light should have been allowed to fall on the plant during one second, in order to give the same amount of light as in the experiment.

I (Exposure).		II (Intensity of light).	III (Candles-seconds).
13	hours	0,000439 H.C.	20,6
10	„	0,000609 „	21,9
6	„	0,000855 „	18,6
3	„	0,001769 „	19,1

I (Exposure).		II (Intensity of light).		III (Candles-seconds).
100	minutes	0,002706	H.C.	16,2
60	,,	0,004773	,,	17,2
30	,,	0,01018	,,	18,3
20	,,	0,01640	,,	19,7
15	,,	0,0249	,,	22,4
8	,,	0,0498	,,	23,9
4	,,	0,0898	,,	21,6
40	seconds	0,6156	,,	24,8
25	,,	1,0998	,,	27,5
8	,,	3,0281	,,	24,2
4	,,	5,456	,,	21,8
2	,,	8,453	,,	16,9
1	,,	18,94	,,	18,9
2/5	,,	45,05	,,	18,0
2/25	,,	308,7	,,	24,7
1/25	,,	511,4	,,	20,5
1/55	,,	1255	,,	22,8
1/100	,,	1902	,,	19,0
1/400	,,	7905	,,	19,8
1/800	,,	13094	,,	16,4
1/1000	,,	26520	,,	26,5

It follows at once from columns I and II that with a shorter exposure the strength of the light has to be increased, in order to obtain a curvature. The calculated values in column III show, in addition, that the intensity of light is inversely proportional to the length of exposure, or, in other words, that a definite quantity of light, independent of the exposure-time, is required to produce a reaction. It is true that the values in column III are not identical, but they clearly oscillate about a mean. Perfect identity cannot be expected in experiments of this nature, when it is remembered that the limit between curvature and non-curvature cannot always be determined exactly; moreover the oats seedlings are of course subject to individual variations, which could only be eliminated by making for each determination a long series of experiments; finally external conditions of humidity, temperature, etc. could not be kept perfectly constant in the various experiments.

There was not much point in choosing exposures of less than 0.001 second, nor of more than 13 hours, since the results obtained show clearly that the essential condition for the production of a phototropic curvature is the supply of a definite quantity of radiant energy; whether this quantity be supplied in a very short time, or only extremely slowly, is a matter of indifference. This result is therefore in complete agreement with PFEFFER's view (at least as far as luminous stimuli are concerned) that the action of a stimulus is to be regarded as a phenomenon of "Auslösung".

A similar critical value for the stimulus has also been observed for the human eye. It is certainly very difficult to compare human observations with reactions of plants under the influence of light, but the observations of BLOCH and CHARPENTIER nevertheless indicate a close analogy between the two sets of phenomena. This is most readily shown by quoting a paragraph from the latter author[1]:

"Nous avons vu le minimum perceptible varier pour des durées de l'excitation allant de $^{2}/_{1000}$ à $^{125}/_{1000}$ sec. Dans ces conditions le minimum perceptible varie toujours sensiblement en raison inverse de la durée de l'excitation. Si la lumière est intense, elle produira cet effet en moins de temps, si elle est faible, elle devra, par contre, durer davantage. Pour que la sensation se produise il faut que, sur une zone rétinienne donnée et dans un certain temps, il arrive pour ainsi dire *une masse constante de lumière,* peu importe que cette masse se distribue sur un grand ou sur un petit espace et qu'elle arrive vite ou lentement sur la rétine. C'est là un fait important, dont il conviendra de rechercher les analogies sur d'autres territoires sensoriels."

From observations, published by BACH[2]) we may perhaps deduce, that something of the same nature holds good for geotropic curvatures as has been found by Mr. BLAAUW for phototropic ones. I hope that further investigations in my laboratory will bring certainty on this point.

Utrecht, September 1908.

ERRATUM.

p. 62 l. 12 from the top: for *uniform* read *uniformly*
p. 183 l. 14 „ „ „ after „*hydrogen line*" insert *C*

(October 28, 1908).

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[1] CHARPENTIER. Archives d'Ophthalmologie. X. 1890, p. 122—123.

[2] H. BACH. Ueber die Abhängigkeit der geotropischen Praesentations- und Reaktionszeit von verschiedenen Aussenbedingungen. Jahrb. für wiss. Botanik. Bd. XLIV. 1907, p. 86.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETINGS
of Saturday October 31, 1908.

(Translated from: Verslag van de gewone vergaderingen der Wis- en Natuurkundige Afdeeling van Zaterdag 31 October 1908, Dl. XVII).

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Geology. — "*On the behaviour of fossil shells in water containing carbonic acid.*" By Dr. P. Tesch. (Communicated by Prof. S. Hoogewerff).

(Communicated in the meeting of September 26, 1908).

It is a well-known phenomenon that all strata which are more or less calcareous and are situated above the surface of the ground-water, when not consisting of wholly impenetrable clay, are exposed to a slow action of solution. The explanation of this extraction of lime is easily given by the dissolving action of the penetrating rain-water, by which the quantity of lime is gradually withdrawn from the higher parts of the deposit and in some cases is concentrated in the lower parts in marl-puppets (for instance in the löss), in other cases however is totally carried off (as a boulder-marl can be transformed in a clay without any lime). The rain-water contains already a good deal of oxygen and carbonic acid ; the part that sinks away in the bottom still takes up the carbonic acid which is formed in the upper-crust by the putrefaction of the vegetable rests and thus it is enabled to exercise an oxidating action on the iron-containing minerals and a dissolving action on the present lime.

Especially the fossiliferous glauconitic sands are totally changed by this alteration. In the first place the glauconite is dissected and the iron which for a great part exists already in the ferri-form, is separated as limonite and forms a binding for the grains of sand. The sand in the beginning of a dark or light green changes into a yellow or brown sand, which in some cases is bound so strongly that the name of a limonite sandstone may be given. Everywhere where glauconitic sands are situated above the surface of the ground-water and are not covered by protecting clay-beds, this phenomenon can be observed. In the southern parts of the Lower Rhine basin for instance the upper-oligocene sea-sands show everywhere where they have kept their original niveau, a yellow or brown colour by the disintegration and oxidation of the glauconite grains (heaved block of Myhl between Hückelhoven and Birgelen on the eastern bank of the Roer, the sandquarries of Gerresheim, Grafenberg and Rothenberg east of Dusseldorp etc.). In Belgium the "sables et grès ferrugineux de Diest", the "Crag jaune d' Anvers" etc. are so converted glauconitic sands.

In the second place however the water with carbonic acid acts as a solvent upon the lime shells of the fossils, which disappear totally or rest as printings and stones and are more difficult to determine, in consequence of which the direct remedy of fixing the age fails or at least becomes uncertain. Especially in Belgium the division of the upper-tertiary deposits has given rise to many contradictions during a long time because the incomplete and indistinct fauna opposed the question of the exact parallelism with similar strata in a high degree. Only by the extensive researches of E. VAN DEN BROECK and others in the Antwerpian pliocene, when those deposits were uncovered on a large scale by the establishment of harbours and docks, this alteration was recognized as a general secondary action which appears everywhere where the circumstances of penetrable cover and a situation above the level of the ground-water allow it. The limit between the decomposed glauconite sand (yellow crag) and the original sand (gray crag) is not at all to be considered as a geological limit but denotes only the level of the ground-water.

I have mentioned these well-known facts in order to arrive at another observation which was made by inquiring the altered deposits and for which an acceptable explanation was ready. It was fixed that the resistance of the different shells against the dissolving action was a different one and thus more and less resisting shells were to be distinguished. The still recognizable stones and printings belonging to the genera Terebratula, Ostrea, Pecten, etc. and these shells being known to consist of calcite, while the small gastropoda shells are composed of aragonite, it was concluded that *calcite is dissolved in water containing carbonic acid with much more difficulty than aragonite.* In the "Handbuch der Palaeontologie" of KARL A. VON ZITTEL (Volume II, page 12) for instance this is expressed as follows:

"Die Kalkspathschalen zeigen eine ziemlich beträchtliche, die Aragonitschalen eine sehr geringe Widerstandsfähigkeit gegen die auflösende Thätigkeit kohlensäurehaltiger Gewässer. In Ablagerungen, wo fast alle fossilen Muscheln oder Schneckengehäuse zerstört und nur durch Steinkerne angedeutet sind, findet man wohlerhaltene Schalen von OSTREA, PECTEN, PINNA, TRICHITES, u. a."

I do not know whether this fact ever has been examined by experiments upon the pure minerals. The failing of any communication concerning that subject in different mineralogical test-books suggests that this has not taken place and thus it may be useful to examine this different behaviour experimentally, so far as the difference of solubility has an importance for the practical geology [1].

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[1] Some time after having finished this communication I got acquainted with an essay of H. W. FOOTE: Ueber die physicalisch-chemischen Beziehungen zwischen Aragonit und Calcit (Zeitschrift für physikalische Chemie, Band 33, pag. 740) to

A. Solubility of calcite and aragonite in pure water.

In all following experiments were used: for calcite fragments of the calcite of Iceland and for aragonite crystals of Bilin in Bohemia.

By pulverizing and sieving a powder was obtained the grains of which were all smaller than 2 mm. and larger than 1 mm. in order to equalize the circumstances.

To compare the solubility of the two minerals in pure water, a quantity of 1 or 2 grams of this powder was exposed during a week to 200 cm^3. of newly distilled water and afterwards the quantity was again weighed accurately.

I obtained the result that the same quantity of pure water in the same time dissolved:

from the calcite powder:

4,8	milligrams
5,0	,,
5,1	,,

and from the aragonite powder:

2,8	milligrams
3,0	,,
3,2	,,

On these numbers a remark is to be made, to which prof. Dr. G. A. F. Molengraaff drew my attention. The grains of calcite will have the form of the cleavage rhomboeder and will moreover show small internal fissures. This has the consequence that the attackable surface offered by the calcite powder is much larger than that of the aragonite powder.

For this reason I experimented another time with the finest powder of the two minerals which had passed a silk sieve of 64 openings on the m.M.^{2}. I acted during the same time with the same quantities.

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which Prof. Dr. S. Hooghwerff drew my attention. According to the law that of two forms the least soluble is the most durable, the author finds in different ways that under the normal circumstances of pressure and temperature calcite is more durable than aragonite. Formerly it had already been shown by experiments of Kohlrausch and Rose that at the temperatures between 2° and 34° C. calcite is somewhat less dissoluble in water than aragonite. The author finds the same fact at the temperatures 25°, 50° and 59° C. By means of the electric properties the difference in solubility in water containing carbonic acid is examined at the temperatures of 8°, 25°, 41° and 48° C. At 49° C. aragonite is still 11 $^0/_0$ more soluble than calcite, though the difference becomes smaller at rising temperature.

The relations of solubility found in this essay agree satisfactorily with the results found by me by direct weighing.

The result was that was dissolved:
from the finest calcite powder: 4,— milligrams
and 4,1 „
from the finest aragonite powder: 5,4 „
and 5,7 „

The quantities of dissolved mineral are very small and so the inaccuracies of the weighing have a great influence. Though these numbers cannot have an absolute validity, I hold myself authorized to say, that *an important difference in solubility does not exist.* Spoken practically calcite and aragonite are both nearly insoluble in pure water. The number found for calcite agrees sufficiently with the knowledge that 10000 parts of pure water dissolve 0,2 or 0,25 parts of calcite.

B. Solubility of calcite and aragonite in water containing carbonic acid.

The solubility in water containing carbonic acid in the form of bicarbonate depends on the duration of the action and on the strength of the dissolving liquor or on the quantity of carbonic acid. I always prepared the liquor immediately before adding the mineral powder, by leading through 200 cM^3 of distilled water a slow current of pure carbonic acid during twenty minutes and by closing the glasses during the experiment. So the strength of the liquor may always have been the same.

I obtained the result that 200 cM^3 of water containing carbonic acid had dissolved after one week:
from the coarse calcite powder: 54,7 milligrams
from the coarse aragonite powder: 61,8 milligrams

The same quantity of the liquor had dissolved after two weeks:
from the calcite powder: 76,5 milligrams
from the aragonite powder: 86,2 milligrams
and after four weeks:
from the calcite powder: 108,4 milligrams
from the aragonite powder: 122,4 milligrams

For the same reason as is mentioned sub *A*, a second series of experiments was made with the finest powder of the two minerals.

200 cm^3. of water containing carbonic acid had dissolved after one week:
from the finest calcite powder: 267,8 milligrams
from the finest aragonite powder: 332,8 milligrams

From these numbers I conclude:

1. *that indeed aragonite is dissolved a little faster by water con-*

taining carbonic acid than calcite. At the same time it is evident however that the difference of solubility is too small to serve for a practical remedy of determination.

2. that this little difference is not sufficient to explain the different behaviour of the fossil lime-shells, but that we must be taken into consideration still other causes: the long duration of the dissolving action, the continuous supply of new liquor, the absolute size of the shells and the relative size of the outer surface.

One finds in the common test-books the notice that 100 grams of water containing carbonic acid dissolve 0,1 or 0,12 grams of calcite which agrees sufficiently with the number mentioned above [1]).

When examining the mineralogical composition of some shells, the question rose what remedy is the most suitable to distinguish calcite from aragonite practically. The little difference in hardness is of no use to this purpose, as a small quantity of silex may neutralize this difference. A calcite shell for instance may equal locally the hardness of aragonite by mixed silex and a determination depending only on this property seems precarious. Nor is the specific weight to be used as a certain quantity of silex, phosphatic lime, magnesia carbonate and organic materials influences it. On the contrary the test with dilute cobaltcarbonate solution of W. Meigen is very useful (Centralblatt für Mineralogie, Geologie und Palaeontologie, Jahrgang 1901, Seite 577). With the aid of this test I examined a number of shells of the following genera, availing myself in some dubious cases of the optical properties.

Of *calcite* consisted:

Ostrea (recent, pliocene and senon)
Pecten (recent, pliocene and senon)
Pectunculus (miocene)
Arca (miocene)
Nucula (miocene)
Leda (miocene)
Venus (miocene)
Cytherea (miocene)
Isocardia (miocene)
Littorina (recent)
Buccinum (recent)
Aporrhais (miocene)
Ancillaria (miocene)

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[1]) Here it must still be added that all these experiments took place at the common chamber temperature (15° or 20° C.) and that the glasses were shaken once a day in order to promote the action of the dissolving liquor.

Of *aragonite* consisted:

Cardium (recent and pliocene)
Ensis (recent and pliocene)
Donax (recent and pliocene)
Tellina (recent and pliocene)
Astarte (pliocene)
Cardita (pliocene)
Cytherea (recent)
Venus (recent)
Unio (recent)
Mactra (recent and pliocene)
Mya (recent)
Corbula (recent and pliocene)
Pholas (recent)
Scalaria (recent)
Natica (recent)
Cypraea (recent)
Turritella (miocene)
Cancellaria (miocene)
Cassidaria (miocene)
Cerithium (recent)
Murex (recent)
Conus (recent and miocene)
Trochus (recent)
Turbo (recent)
Bulla (recent)
Strombus (recent)
Ficula (recent)
Terebra (recent, miocene)
Niso (miocene)
Dentalium (pliocene, miocene and oligocene)
Ringicula (miocene)

On looking through the above list it is evident that a great deal of the examined Lamellibranchiata consists of aragonite though among the fossil species enough calcite shells occur. A specimen of the miocene Cytherea incrassata consists without any doubt of calcite and a specimen of the recent Cytherea meretrix consists with the same certainty of aragonite. Such was also the case with the miocene Venus multilamellosa and the recent Venus albina. Among the Gastropoda shells the majority consists of aragonite but four shells form an exception. For the fossil specimina of Aporrhais and Ancillaria perhaps it is permitted to think of a later inversion of aragonite into calcite but for the very new specimina of Buccinum undatum and Littorina littorea this explanation seems excluded. Possibly the form in which the lime carbonate is separated depends on external influences and a species which builds as a rule an aragonite shell may be able to separate calcite under abnormal circumstances (temperature, composition of the water). This appears to me the more probable as we can precipitate artificially calcite or aragonite according to the circumstances of temperature and composition of the solution. If this should be true the composition of the shell is no specific property.

Geophysica. — "*Earthcurrent-Registration at Batavia.*" (3^d communication). By Dr. W. van Bemmelen.

In the preceding communication about my earthcurrent registration in Java, I expected to be able before long to throw more light on the question of the abnormal intensity of the current between Batavia and Anjer (a place in the neighbouring residency of Bantam)

The kind co-operation of the Superintendent of Government Railways, who allowed me the use of the railway telegraph lines during night time, enabled me to realise my intention of measuring the currents flowing between Batavia and some other places situated in the residencies of Batavia and Bantam.

In order to obtain an exact control over the new results, I registered next to the currents flowing through these wires, those between Anjer and Batavia flowing through the direct telegraph line between these towns, i.e. by means of the line formerly used by me. Moreover the N—S component of the magnetic force was recorded.

By means of the railway telegraph-wires I obtained connection with the following places:

Laboean on the Westcoast of Java, 32 K.M. to the S.S.W. of Anjer.

Serang 28 K.M. to the East of Anjer.

Rangkas Betoeng 40 K.M. to the East of Laboean.

Between Anjer, Serang, Rangkas Betoeng and Laboean there rises a volcanic chain, the volcano Karang (1780 M.) being the culminating summit.

Tangerang 21 K.M. to the West of Batavia.
Bekassi 20 ,, ,, ,, E.S.E. ,, ,,
Krawang 54 ,, ,, ,, E.S.E. ,, ,,

The directions and distances from Batavia are:

Batavia—	Anjer	W 5°N.
„	Laboean	W 12 S.
„	Serang	W 4 N.
„	Rangkas Betoeng	W 17 S.
„	Tangerang	W 1 S.
„	Bekassi	E 17 S.
„	Krawang	E 14 S.

I think it necessary for a better understanding of the results to be mentioned hereafter, to summarise the results obtained before.

In my former work on earthcurrents I always compared the oscillations shown in the intensity of the current, with those occurring simultaneously in the magnetic component, always taking into account the horizontal component directed perpendicularly on the straight line connecting the two stations.

I measured the variations of the magnetic component in absolute measure, and determined those of the earthcurrent by means of the differences of potential per Kilometer, which, if existing, should give the same variation of the current through the wire as was shown by the recording galvanometer.

Thus I did not decide whether such a difference of potential really existed at the two stations.

The records obtained brought to view the fact, that especially for places one of which lies to the East of the other, each oscillation of the earthcurrent corresponded with a simultaneous one of the component. But if one station lies to the North of the other the correspondence with the E.-W. component of magnetic force was much less than in the former case.

The connection between corresponding oscillations of earthcurrent and magnetic force may be described thus. Those of the earthcurrent precede those of force with a certain difference of phase; their amplitude increases compared with those of force, when the duration decreases.

As to the amount of this difference of phase and of this increase of amplitude I found them to be quite different for the coast-plains of North-Java and the volcanic regions in the southern part of the island.

In the South especially the increase of amplitude, which accompanies decreasing duration, was much more rapid, than in the northern regions. The following figures will make this divergence evident.

Mean half duration of the oscillation	Amplitude of earthcurrent in volts. per K.M. / Amplitude of magnetic force	
	Northern-Java Batavia-Cheribon	Southern-Java Buitenzorg-Tasik Melaja
0.5 min.	21.2	59.0
1.2 „	20.5	55.0
9 0 „	16.5	15.0

I recorded the current between Semarang and Cheribon and between Semarang and Soerabaja during a stay at the former place and found it to be of the same type and strength as the current between Batavia and Cheribon. The current between Batavia and Anjer however, though bearing also this same type, I found to be more than four times stronger. Experiments made specially for that purpose giving evidence of the reality of this phenomenon, the next step to be done was to examine the current between Batavia and other places situated between Anjer and Cheribon. In the months of March and April of this year I made these measurements, having recorded during some nights the current for each station in connection with Batavia, together with the Batavia—Anjer current and the N—S component of magnetic force.

I measured on the diagram obtained the amplitudes for a certain number of oscillations of short and of longer duration; the average values are given below. For each case I have added the proportion of the strength of the currents (per K.M.) to that of the Anjer-current. (See table p. 245).

When we examine the numbers of the last column, which give the proportion of the strength of the currents between Batavia and Anjer we at once see that for each case this proportion is nearly the same for shorter and longer oscillations (only for Batavia-Bekassi we find an exception, the numbers being 1.9 and 1.3 resp.).

Now this means that also for different regions between Anjer and Cheribon the currents bear the type of the coast-plains of northern Java, as was mentioned above.

But the numbers also point to a gradual increase of strength, when we connect successively Batavia with places of an increasing westerly position.

Supposing the current between Batavia and Cheribon to be 1.0,

Earth-magnetical E-W component		Earth-current				
Half duration of the oscillation	Amplitude	Amplitude of the Earthcurrent in V.p. KM. / Ampl. of the magn. force in abs. meas.				Ampl. Btv.-Anjer / Ampl. Btv.-Station
1.3 min.	1.27	Batavia—Laboean	71	Batavia—Anjer	83	1.2
7.3	2.8	„ „	60	„ „	62	1.1
0.5	1.6	Batavia—Serang	86	„ „	97	1.1
2.0	0.9	„ „	66	„ „	75	1.1
9.6	3.3	„ „	57	„ „	68	1.2
0.9	0.5	Batavia—Rangkas Betoeng	80	„ „	82	1.0
10.0	1.2	„ „ „	52	„ „	47	0.9
0.5	1.0	Batavia—Tangerang	49	„ „	97	2.1
6 2	0 8	„ „	39	„ „	82	2.0
0.5	0 9	Batavia—Bekassi	47	„ „	89	1.9
13.7	7.5	„ „	43	„ „	57	1.3
0.7	0.4	Batavia—Krawang	25	„ „	93	3.7
13.7	2.8	„ „	20	„ „	72	3.6
		Batavia—Cheribon				4.2

we have, taken into account the variations of the current during short oscillations only :

	Amplitude Earthcurrent
Batavia—Cheribon	1.0
„ Krawang	1.1
„ Bekassi	2.2
„ Tangerang	2.0
„ Rangkas Betoeng	4.2
„ Serang	3.8
„ Anjer	4.2
„ Laboean	3.5

If we suppose, that a difference of potential rises between Cheribon and Batavia, when a certain variation of the magnetic force occurs, and supposing the gradient of potential to be 1 Volt per K.M., we are able to calculate the potentials rising at the different stations.

For convenience, sake we may assume the potential at Cheribon to be zero. We find:

Laboean	595	volt
Anjer	645	„
Serang	496	„
Rangkas Betoeng	481	„
Tangerang	242	„
Batavia	200	„
Bekassi	156	„
Krawang	141	„
Cheribon	0	„

From these and formerly found values we deduce the following gradients.

Between	Potent. gradient	Geological formation.
Anjer and Serang	5.3	Neo-volcanic
Serang and Tangerang.	4.5	Quaternary
Rangkas Betoeng and Tangerang	4.1	Quaternary
Tangerang and Bekassi	2.1	Quaternary and alluvium
Bekassi and Krawang	0.4	Alluvium
Krawang and Cheribon	1.0	Quaternary and alluvium
Cheribon and Semarang	0.9	Quaternary and cretaceous
Semarang and Soerabaja	1.1	Quartenary, cretaceous a. alluvium.

The geological formations encountered on the different passages, have been borrowed from the geological atlas of Verbeek and Fennema.

It is not to be denied, that a certain connection seems to exist between gradient and formation, such that the gradient is least in alluvium, greater in quaternary and greatest in the volcanic layers; and neither may it be said, that this succession is improbable.

Also for the volcanic province of the Preanger in southern Java I found a high value, viz. 3, but here the proportion of amplitudes for current and force bears the other type, which involves the gradient to be small, viz. 1, for oscillations of longer duration.

The formations given by the geological atlas are those met with at the surface of the earth, and the outlines of the deeper layers, no doubt, will differ much from those of the superficial ones.

Thus when we find a connection between the strength of the current and the outlines of the superficial layers, this points out that the currents measured are the superficial ones too.

Accordingly it is no wonder that the currents bear a different type in the mountainous Preanger compared with those of the coast-plains; but I utterly fail to explain this difference, just as it has been found.

All that has become known till now points to the next step, which should be taken in this research, viz. that the earth-connections should be brought to a depth of, say one or more kilometers under the surface of the earth, but, alas this is impossible.

It is true I had the intention to make use of two artesian wells to be bored recently at Serang and Batavia, but the considerations, that first the mantle of these holes consisted of iron, the depth was only 0,2 à 0,3 K.M., and besides the wire connecting the two did not possess the necessary isolation, frightened me out of this burdensome experiment.

I think it advisable to continue the registration in the old way, but to take into account the geological formation in the first place.

Dr. L. Steiner of Budapest has directed my attention to the fact, that I have erroneously applied the formula $A = 0.8 \sqrt[4]{\frac{1}{TM}}$ (c.f. 1st Comm. Proc. Jan. 25, 1908. p. 515) on the harmonic terms of the daily variation for the earthcurrent between Batavia and Cheribon.

Indeed a calculating error has curiously given rise to an apparent agreement between the observed values and those computed by means of the formula.

Dr. Steiner deduced the following expression

$$\frac{A}{M} = 3.9 \, \frac{1}{T^{0.8}} \text{ or } \frac{A}{M} = 3.9 \, \frac{T^{0.2}}{T}.$$

This formula gives the following values

	Amplitude				
	Earth-current volt. p. KM. × 10^{-5}	Magn. Comp. c. g. s. × 10^{-5}	Earth-current / Magn. comp. Observ.	Earth-current / Magn. comp. Calc.	Δ C—O
A_1	74.6	18.62	4.0	3.9	— 0.1
A_2	43.8	7.63	5.7	6.6	0.9
A_3	27.7	2.96	9.4	8.9	— 0 5
A_4	8.9	0.90	9.9	10.8	0.9
A_5	6.9	0.53	13.0	13.0	0.0
A_6	6.6	0.42	15.7	15.0	— 0.7

He also remarks that this formula agrees in character with my theoretical one, viz.

$$\frac{A}{M} = C \frac{\varrho}{1 + c'} \cdot \frac{1}{T}$$

because $1 + c'$ slowly increases with decreasing T.

This, indeed is the case. For instance when we assume $\varrho = 3.70 \times 10^{13}$ or $\sigma = 10$, and consider the spherical function of order 2 we find after SCHUSTER (Phil. Tr. Vol. 180 p. 496):

σ	$1 + c'$	$\underbrace{\frac{1 + c'}{1.172}}$
1	1.019	$0.869 = 0.1^{0.061}$
5	1.093	$0.933 = 0.5^{0.100}$
10	1.172	1.000 —
20	1.278	$1.091 = 2^{0.126}$
30	1.337	$1.141 = 3^{0.120}$
40	1.374	$1.173 = 4^{0.115}$
50	1.399	$1.194 = 5^{0.110}$
100	1.466	$1.251 = 10^{0.097}$

The exponent accordingly changes slowly, and reaches as a maximum 0.126, a value, which approaches the value 0.2 required by the empirical formula.

I think this points to a possibility to bring agreement between the theoretical assumptions and the observed facts for the daily variation of earth-current and magnetic component. However this is not the case for the short osciliations.

I regret that my near return to Europe prevents me from entering now on those questions, or making new experiments.

Batavia, Aug. 1908.

Chemistry. — "*The nitration of toluene*", by Prof. A. F. HOLLEMAN.

(Communicated in the meeting, of September 26 1908).

On account of its great technical importance the nitration of toluene has been studied repeatedly; the determination of the quantity of *o*- and *p*-nitrotoluene contained in the product of the reaction has also been carried out a few times. RAOUL PICTET, (C.r. **116**, 815) states that when toluene is nitrated at — 55° 5.5 times as much *p*-nitrotoluene is formed as when the nitration is carried out at 0°. HOLDERMANN, (B. **39**, 1250) tried to modify the proportions in which *o*- and *p*-nitrotoluene are formed by adding catalyzers (generally consisting of metallic salts) to the mixture of nitric and sulphuric acid used in the nitration. The amount of *o*-nitrotoluene present in the product of nitration only varied however from 57.16 to 60.85°/₀. In these experiments the temperature was kept between 5 and 10°. When nitrated at 0° with nitric acid (sp. gr. 1.52) 52.7°/₀ of nitro-toluene was obtained; on addition of different salts (the proportions are not stated) to this acid the quantity of *o*-compound diminished and when nickel sulphate was added it even got as low as 45.5°/₀.

Friswell, (C. Bl. 1908[1], 2092) nitrated toluene under many various conditions in order to increase the yield of *p*-nitrotoluene. He obtained however, always 60—65°/₀ of *ortho*- and 40—35°/₀ of *para*-compound.

None of these chemists make any statement as to the method used in these determinations, although Holdermann expresses his results even in two decimals. As will be noticed from the above quotations the figures differ widely. Moreover, Nölting (B. **12**, 443; **18**, 1337) has shown that the nitration product of toluene contains *m*-nitrotoluene the amount of which he estimates at 1—2°/₀. It is, therefore, obvious that there is, as yet, no question of a fairly accurate knowledge as to the composition of the product of nitration of toluene, and, for this reason, I instructed Mr. van den Arend to determine the composition, with the aid of the more accurate methods, which for that purpose have been worked out in my laboratory. In this particular case the method of the solidifying points was the most practical one.

In order to apply the same, it is necessary to procure, first of all, the three *mono*nitrotoluenes in an absolutely pure condition. A preparation of *o*-nitrotoluene of great purity has been obtainable for the last few years from Meister, Lucius and Brüning. A specimen received previously from that firm still contained 0.4°/₀ of *p*-nitrotoluene (These Proc. VII, p. 395). At my request they were kind enough to once more purify a sample of this almost pure *o*-nitrotoluene by freezing, and to place two kilos of the purified preparation at my disposal, for which I express to that firm my sincere thanks. This was found to contain only 0.13°/₀ of *p*-nitrotoluene and was used by Mr. van den Arend in his experiments without any further purification, except a single distillation in order to remove the dissolved water; a correction was then applied for the *p*-compound content.

It was shown that the methods proposed by Reverdin and la Harpe (Beilsteins Handbuch II, 91) and by Loesner, (J. pr Chem. (2) **50**, 567) to free *o*-nitrotoluene from any *p*-nitrotoluene present are quite useless. *o*-Nitrotoluene is dimorphous; the melting points of the two modifications were determined by van den Arend by means of his preparation and found to be — 3°.7 and — 9°.4. According to his observation the unstable modification with the higher m.p. is formed most readily when the liquid substance is cooled rapidly to about — 30°. First, a solid yellowish mass is formed, which, on further lowering of the temperature, begins to show white spots and then turns quite white, with production of a crushing sound; the crystalline mass thus obtained melts at about — 4°.

m-Nitrotoluene is obtainable from de Haen in a very pure condition. It was fractionated a few times when the melting point was found to be + 16° and the boiling point 230—231° at 756 mm.; it may therefore, be taken as pure.

p-Nitrotoluene from Kahlbaum was recrystallised twice from alcohol and then distilled in vacuo; its solidifying point was found to be 54°.4.

Solidifying curve of o- and p-nitrotoluene.

°/₀ *para*-nitrotoluene	initial solidifying point	end solidifying point
100.0	+ 54°.4	—
97.5	50°.0	—
91.6	46°.2	—
79.0	38°.5	—
72.9	33°.8	—
67.5	30°.4	—
60.5	24°.4	—
46.6	11°.6	— 15°.0
42.3	5°.4	15°.2
39.8	1°.8	15°.7
37.2	— 1°.2	14°.6
33.5	6°.8	—
30.6	14°.8	—
24.9	14°.4	15°.6
16.3	12°.1	—
11.2	11°.3	—
0.0	0°.4	—
		mean — 15°.2

Fig. 1 represents the solidifying curve constructed with the aid of these figures.

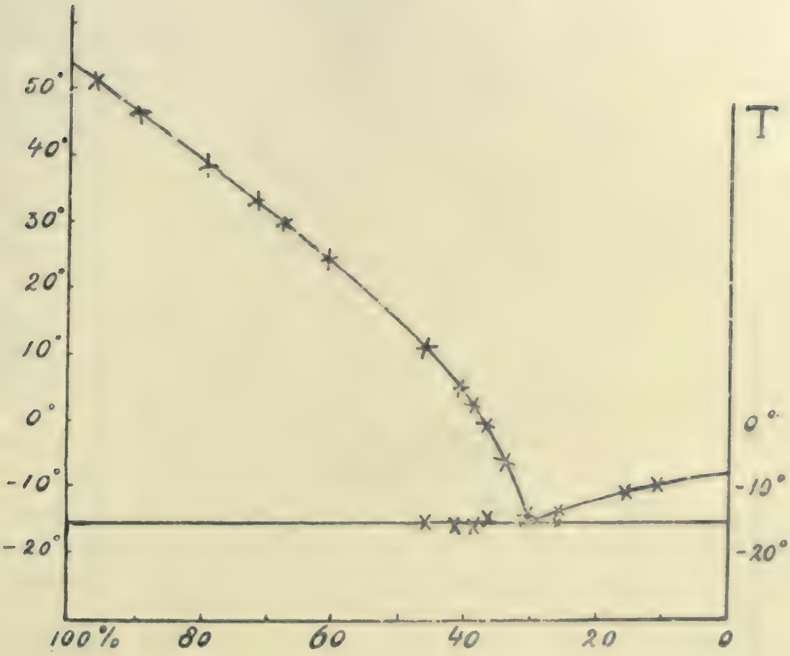

Fig. 1. Melting point curve of *o*- and *p*-nitrotoluene.

Mr. VAN DEN AREND found the following figures for the specific gravities of *o*- and *p*-nitrotoluene and for some of their mixtures, at 80°.0:

100 %	*p*-nitrotoluene . . .	1.0981	calculated from the sp. gr. of *o*- and of *p*-nitrotoluene
89.4 „	„	1.0993	
68.4 „	„	1.1007	
61.0 „	„	1.1014	1.1006
46.5 „	„	1.1023	1.1015
32.0 „	„	1.1033	
0.0	(100 % *o*-nitrotoluene . .	1.1045 [1])	

The figures calculated are those which may be deduced from the specific gravities of the isomers without contraction taking place. The graphic representation of these figures gives the subjoined diagram which plainly shows the contraction which takes place on mixing the isomers, by the higher sp. gr. which the mixtures possess, in comparison with the calculated values (the straight line).

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[1] Dr. S. VAN DORSSEN has also at my request determined the specific gravities of *o*- and *p*-nitrotoluene by means of an EYKMAN's pycnometer verified by himself and found as the average result at 80°.0 of four and three determinations respectively: *o*-nitrotoluene 1.1050; *p* nitrotoluene 1.0993, values which are both a little greater than those of VAN DEN AREND. All the values have been corrected for vacuum and the expansion of the glass. I will, however, use V. D. AREND's figures because he has made all his determinations with the same pycnometer and therefore the results are sure to be mutually comparable.

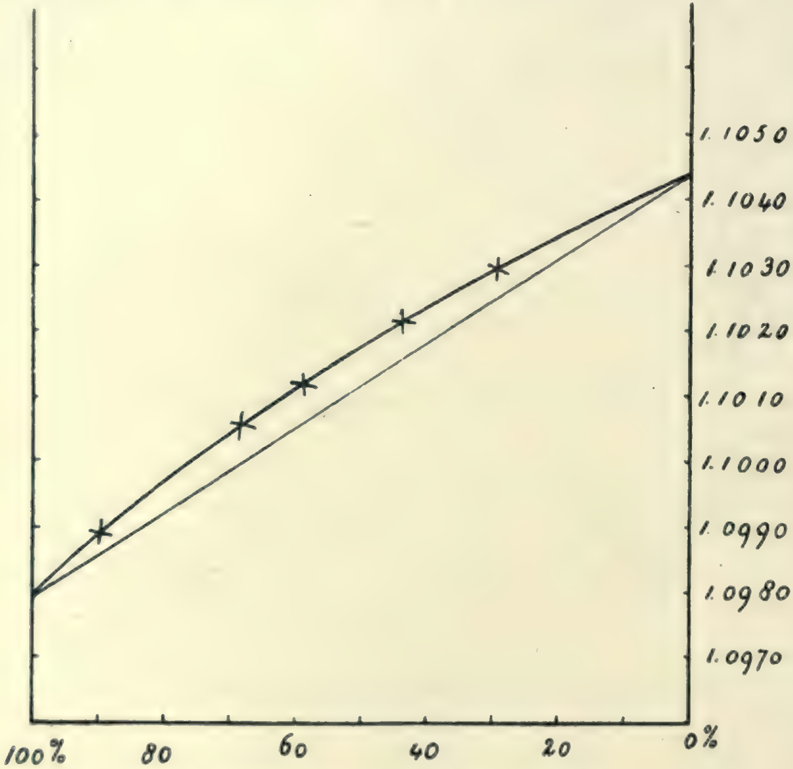


Fig. 2. Line of the specific gravities of *ortho-* and *para*-nitrotoluene.

The nitration of toluene was carried out by the method of Beilstein and Kuhlberg, (A. **158**, 348), i.e. the nitric acid being added to the toluene and not reversedly, because, by their method, the formation of dinitro-products is entirely avoided. The toluene employed had a constant boiling point (110°.8 at 760 mm.) and had been purified by being boiled with sodium wire in a reflex apparatus.

The nitration of the purified toluene took place at the temperature of — 30°; 0°; + 30° and + 60° and was carried out as follows:

75 grams of the toluene were placed in a small flask and brought to the required temperature. 200 c.c. of nitric acid (sp.gr. 1.475) were slowly dropped into the toluene, the mixture being stirred mechanically. Immediately after the addition of the first drops of the acid the liquid turned intensely brownish-red; so that it was not possible to see whether two liquid layers or one homogeneous mixture was formed. The heat evolved during the nitration was but trifling, at

least at 0°. After some time, the mixture was shaken repeatedly in a large separation funnel with water until no more acid reaction could be observed.

Being dried over sodium sulphate, the product was distilled in vacuo. The temperature was first kept for some time at 40°, to remove any unattacked toluene; at a pressure of 1 to 2 m.m. and a temperature of 90°—100° the whole distilled over leaving but a very small residue. Towards the end of the distillation much of the *p*-nitrotoluene passed over, which deposited in the exit tube as a yellow crystalline mass.

The distillate consisted of a clear pale yellow liquid.

After the solidifying point and the sp.gr. of such a nitration-mixture had been determined the distillation in vacuo was once more repeated and the solidifying point and the sp. gr. determined again. These did not differ perceptibly from the first ones.

The end solidifying points could also be determined pretty sharply; the subjoined table shows the results obtained:

Nitration at:			Spec. Gr.
— 30°	initial solidifying point	+ 4°.1	1.1026
	end ,, ,,	— 16°.6	
0°	initial ,, ,,	+ 2°.8	1.1026
	end ,, ,,	— 16°.8	
+ 30°	initial ,, ,,	+ 1°.4	1.1027
	end ,, ,,	— 16°.9	
+ 60°	initial ,, ,,	— 0°.8	1.1028
	end ,, ,,	— 17°.4	

The specific gravities were again determined at the temperature of boiling benzene and reduced to 80°.0. They have been corrected for vacuum and expansion of the glass.

I have had these observations repeated in part by Messrs CALAND, VAN DORSSEN and DE LEEUW who have themselves purified toluene in the manner described, nitrated the same, and determined the initial and end solidifying point, also the sp. gr. of their nitration product. They found:

Nitration at:			Sp. Gr.
0°	initial solidifying point:	+ 1°.0 ; + 2°.7	1.1026
	end ,, ,, :	—18°.1 ; —18°.4 ; —18°.2	
60°	initial ,, ,, :	+ 3°.1	1.1023
	end ,, ,, :	— 18°.5	

The end solidifying points were found to be a little lower; as regards the initial solidifying point of + 3°.1 in the nitration at 60° it should be observed that the mixture of toluene and nitric acid had been left over night and separated into two layers which was not the case in VAN DEN AREND's experiment. With an initial solidifying point of — 0°.8 corresponds 37.5 $^0/_0$ of *p*-nitrotoluene; with that of + 3°.1, 40.7 $^0/_0$, disregarding, for the moment, the small quantity of *m*-nitrotoluene present in the nitration product. As a content of 40.7 $^0/_0$ of *p*-nitrotoluene corresponds with a sp. gr. of 1.1026 it seems that no higher nitration products are formed, even at + 60°, when the nitration is carried out in the manner indicated. This is also shown by the position of the end solidifying point which is but little lower than that found with the nitration products obtained at lower temperatures.

In order to determine the *o*-, *m*- and *p*-nitrotoluene content of the nitration product it must be regarded as a ternary mixture, and the lowering which the initial and end solidifying points undergo, on adding a small quantity of *m*-nitrotoluene, should be determined, as NÖLTING's investigation had shown that the latter is present only to the extent of a few $^0/_0$.

A mixture of pure *o*- and *p*-nitrotoluene weighing 2.8319 grams, composed of 35.5 $^0/_0$ *para*- and 64.5 $^0/_0$ *ortho*-nitrotoluene, had an initial solidifying point — 3°.8 and an end solidifying point — 14°.9.

If now 0.0860 grams of 2.9 $^0/_0$, of *meta*nitrotoluene were added, the initial solidifying point fell to — 6°.0, the end solidifying point to — 16°.7.

The percentage of *o*- and *p*-nitrotoluene in the mixed nitration product at 0°, with an initial solidifying point + 2°.8 and an end solidifying point — 16°.8 could now be determined in the following manner, keeping account of the *meta*-compound formed.

On addition of 2.9 $^0/_0$ of *meta* the end solidifying point falls from — 14°.9 to — 16°.7 = 1°.8. Owing to the presence of *meta*-nitrotoluene, the end solidifiying point of the mixed nitration product has been found to be — 16°.8 instead of — 14°.9 (the eutectic point of the mixture *ortho* + *para*), therefore 1°.9 lower. From this it follows that in the mixture at 0° there is present $\frac{1.9 \times 2.9}{1.8} = 3.1\ ^0/_0$ of *meta*.

Owing to the presence of those 2.9 $^0/_0$ of *meta*-compound, the initial solidifying point of the artificial mixture has fallen from — 3°.8 to — 6°.0, therefore 2°.2. For 3.1 $^0/_0$ of *meta* the fall must amount to 2°.4. If for the mixed nitration product is found an initial solidifying point of + 2°.8, this would have been 5°.2 if no *meta*-compound were present, from which it follows that 42.2 $^0/_0$ of *para*- and 57.8 $^0/_0$ of *ortho*-nitrotoluene must have formed.

Applying this manner of calculation to the other mixed nitration products we found them to possess the following composition:

Nitration at			$^0/_0$ *para*	$^0/_0$ *ortho*	$^0/_0$ *meta*
— 30°	initial solidifying point	+ 4°.1	41.7	55.6	2.7
	end „ „	— 16°.6			
0°	initial „ „	+ 2°.8	40.9	56.0	3.1
	end „ „	— 16°.8			
+ 30°	initial „ „	+ 1°.4	39.9	56.9	3.2
	end „ „	— 16°.9			
+ 60°	initial „ „	— 0°.8	38,5	57,5	4.0
	end „ „	— 17°.4			

If the end solidifying point of the nitration product prepared at 0° is taken as 18°.1, namely, the mean of the figures found afterwards, the *meta* content increases and amounts to 5.3 $^0/_0$. There remains, therefore a doubt of about 1 $^0/_0$ in regard to the quantity of *meta* compound present in the nitration product, if on the one hand we accept the mean of VAN DEN AREND's values as the true solidifying points, and on the other hand the average values of the other investigations. But also for another reason the quantity of the *m*-compound cannot be determined more accurately.

In the above calculation various surmises have been made. It is for instance, supposed that, at least over the first course, the line which connects the binary eutecticum of *ortho*- and *para*-nitrotoluene with the ternary eutecticum is a straight line. It has also been taken for granted that the fall of the initial solidifying point is proportional to the addition of small quantities of a third isomer. An exact determination would be possible only when the entire ternary melting figure were constructed; yet the method as applied here gives a satisfactory approximation as will be seen from a survey of Fig. 3.

In the plane OPO′P′ is situated the melting point curve of *o*- and *p*-nitrotoluene. If, however, a small quantity of *m*-nitrotoluene is present we do not determine a point of the melting point curve O′E′$_1$P′, but a point of a curve situated on a line O″E′$_1$P″, which is obtained by carrying through the prism a plane paralell to the OP plane, and this at a distance from the OP plane corresponding with the amount of *meta* present. If an arbitrary mixture M consisting of *o*-, *p*- and *m*-nitrotoluene is cooled a separation of solid *ortho* or *para* will take place at a definite temperature; all depends on whether the mixture has the composition indicated by the right or the left melting point plane. This point B is the initial solidifying point. On further decrease of the temperature the solidification proceeds along a curve

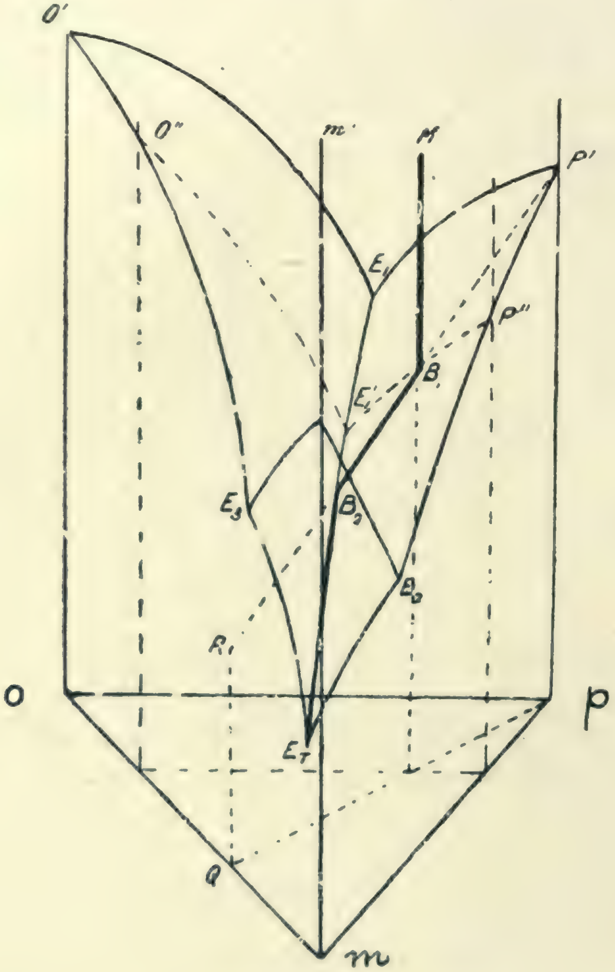


Fig. 3.

B_1B_2 which is obtained by intersection of the melting point plane with a plane PP'QR, passing through Pp' and the point Q indicating the proportion in which *ortho* and *meta* are present. For in that plane the proportion of *o* and *m* does not alter during the cooling while *p* is being deposited. On cooling still further the composition of the liquid is indicated by the points of the line B_2E_T along which *ortho* and *para* both separate; in E_T *meta* also begins to separate and all becomes solid.

If the quantity of *m*-nitrotoluene is small, B_2 is situated very closely to E_1 and the very short line E_1B_2 may be taken as a straight one, of which use has been made in the above calculations.

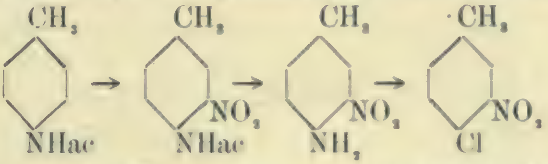
Amsterdam, Org. chem. lab. Univ. Aug. '08.

Chemistry. — "*The nitration of p-chlorotoluene.*" By Prof. A. F. HOLLEMAN.

The *p*-chlorotoluene required for this purpose was prepared by Mr. VAN DEN AREND from pure *p*-toluidine b. p. 160—161° at 754 mm.; m. p. + 7°. Of both nitro-*p*-chlorotoluenes the isomer

$$CH_3, Cl, NO_2 = 1, 4, 2$$

was obtained by him from *p*-chlorotoluene by nitration and separation of the mononitrocompounds; it melted at + 38°. He prepared the other isomer $CH_3, Cl, NO_2 = 1, 4, 3$ according to GATTERMANN's method B. **18**,1483 which may be expressed by the following scheme:



The product obtained had a boiling point of 259—260° at 759 mm. and melted at + 7° in a capillary tube. The solidifying point was + 5°8.

For the determination of the relative quantities of both isomers present in the nitration product of *p*-chlorotoluene the solidifying point determination process was again found to be the most suitable. Hence the solidifying point curve of these isomers had to be determined. Mr. VAN DEN AREND obtained the subjoined figures:

% $2\text{-}NO_2\text{-}4\text{-}Cl$-toluene	Initial solidifying point	End solidifying point
100.0	+ 38°.2	—
57.0	+ 9°.7	—7°.9
44.7	+ 1°.4	—8°.2
34.8	— 6°.3	—
29.8	— 7°.2	—
24.1	— 4°.1	—8°.2
17.5	— 0°.5	—
14.1	+ 0°.4	—
6.6	+ 4°.5	—
0.0 (100% $3\text{-}NO_2$-4-Cl-toluene)	+ 5°.8	—

Of these the following figure is the graphic representation.

For the sp. gravities of both isomers and for some of their mixtures, Mr. VAN DEN AREND found the following figures, corrected for upward air pressures and for the expansion of the glass of the pycnometer. The temperature was 80°.0.

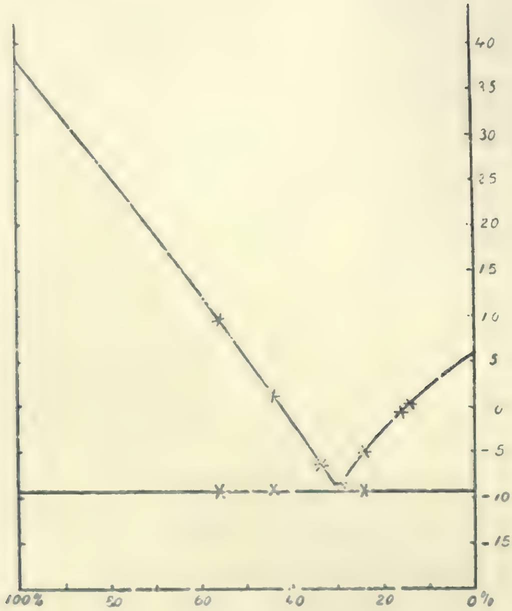


Fig. 1.
Solidifying point line of *p*- and *o*-nitrotoluene.

2-nitro-4-chlorotoluene		calculated
100°/₀	1.2559	
57.0	1.2477	1.2446
17.5	1.2364	
0.0°/₀ (100°/₀ 3-nitro-4-chlorotoluene)	1.2296	

In the subjoined graphic representation they have been united. The calculated value is the one which the sp. gr. ought to have according to the straight line in the figure, so without contraction. The latter is therefore rather considerable.

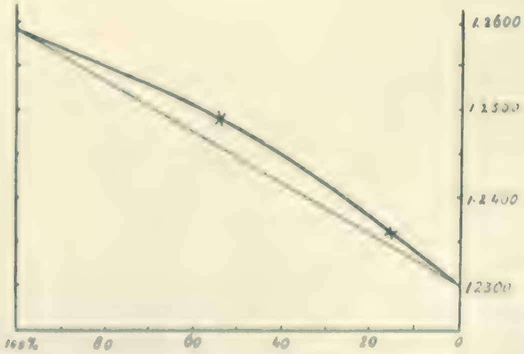


Fig. 2.
Line of the specific gravities for mixtures of the mono- nitro- para- chlorotoluenes.

It was only after some unsuccessful efforts that we succeeded in carrying out the nitration of *p*-chlorotoluene with nitric acid, in that sense that everything was just nitrated, without formation of any dinitro-products. Mr. VAN DEN AREND could ascertain this by determining the specific gravities. As in the case of pure toluene it was again found practical, in order to avoid the formation of higher products of nitration, to add the nitric acid to the *p*-chlorotoluene and not reversedly.

10 grams of *p*-chlorotoluene were cooled to 0°. At that temperature it solidifies to large leaf-like crystals; at the moment of crystallisation setting in, nitric acid (D. 1.48) was added, drop by drop, with thorough shaking. After 1 cc of acid had been added all the crystals had already fused. The liquid turns very dark and consists at first of two layers. After further addition of acid, the temperature being kept at 0° the colour turns pale yellow and the liquid becomes homogeneous. When this point was reached the further addition of acid was stopped and after a few moments the liquid was poured into water. In all, four times the weight of nitric acid was used. The pale yellow oil which collected at the bottom was agitated repeatedly with water until no further acid reaction was noticed, and then dried over sodium sulphate. The following day, the nitration product was distilled twice in vacuo when a slight black residue was left behind. The yield of purified product was 12 grams. It had an initial solidifying point of + 10°.2 and an end solidifying point of − 8°.0. From the first figure it follows that the nitration product must contain 58 % of $CH_3,Cl,NO_2 = 1, 4, 3$, whilst the figure for the end point, which coincides with the eutectic point, shows that the mixture contains no other substances besides these two. This was also proved by the sp. gr. which was found to be 1.2481 for an artificial mixture of this composition, whilst the nitration mixture possessed the same sp. gr. Mr. DE LEEUW who also nitrated *p*-chlorotoluene in the manner described, found the initial solidifying point of his product + 10°.9, the end point − 8.°3. This initial point corresponds with 58.8 % 1.2.4.

Mr. VAN DEN AREND also mixed an artificial mixture of both isomers containing 58 % 1.2.4 and 42 % 1.3.4 with the nitration product in about equal quantities; the mixture so obtained solidified at + 10°.3.

It may, therefore, be taken as proved that the nitration product has the above composition. A chlorine determination according to Carius gave 20.3 % (calculated 20.7 %).

Two nitrations were carried out at + 30° in the manner described, using nitric acid (D. 1.45) which both yielded a product the sp. gr. of which was much too high. It appeared that at this temperature higher substituted nitro-products were readily formed.

If the nitration is carried out at + 60° a product is formed which solidifies at — 9°,2, a temperature which is situated lower than the eutectic one of mixtures of the two pure components. The sp. gr. is 1.2626. No doubt considerable quantities of polyvalent nitro-compounds are formed at this high temperature of nitration.

Amsterdam, Org. chem. lab. Univ. Aug. '08.

Chemistry. — “*The quantitative estimation of the products of nitration of m-chloro and m-bromobenzoic acid.* By Prof. A. F. Holleman.

The above investigation has occupied me more than once. 1) In the nitration of each of these acids two nitrohalogen acids are formed namely 1,6,3 = CO_2H, NO_2, Cl (Br) as main product and 1,2,3 = CO_2H, NO_2, Cl (Br) as byeproduct; the question arose in what proportion these acids are present in the nitration mixture.

The reasons which induced me to revert to this investigation are twofold. Firstly, because the percentage of byeproduct in the nitration mixture of *m*-chlorobenzoic acid was found 2.8 higher in the first investigation than in the second, when another method of analysis was applied and this difference was not satisfactorily explained. Secondly because it was found in the nitration of *o*-chloro- and *o*-bromobenzoic acid and also in that of *m*-chlorobenzoic acid, that more byeproduct is formed at 0° than at — 30°, whereas in the nitration of *m*-bromobenzoic acid the very opposite result was noticed.

In the first investigation the quantity of main product was determined by extracting the nitration mixture with benzene and determining the sp. gr. of the benzene solution. In the second determination the quantity of byeproduct was deduced from the solidifying point of the mixture. A third *modus operandi* was followed for this renewed investigation, namely, the extraction of the nitration mixture with water and titration of the aqueous solution obtained.

I do not intend giving any further details of these methods as I described these repeatedly on former occasions.

Messrs. J. J. Polak and H. L. de Leeuw, who have carried out these investigations independently, started from chemically pure preparations of *m*-chloro- and *m*-bromobenzoic acid, which were nitrated with absolute nitric acid after which the nitration product was collected according

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1) R. 19 188, [1900] and R. 20, 223 [1908].

to the method given in *R.* **20,** 223. I will only add that the complete removal of nitric acid from the product was effected with particular care as it appeared that this acid is retained with great obstinacy. In order to get the nitration product so pure that it gave, at the ordinary temperature, no, or but a feeble reaction with sulphuric acid and diphenylamine, it was necessary to wash it many times with cold water and to dry it over lime in vacuo. The organic acids, which had dissolved in the washings were, of course, recovered in the manner described previously. The removal of the last traces of nitric acid was of great importance in these determinations, because the presence of even very minute quantities of this acid causes, in the analytical method followed here, a too low percentage of the byeproduct.

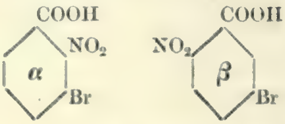
In this method about 0.4 gram of nitration mixture is extracted with 100 grams of water and the acidity estimated by titration with $^n/_{10}$ alkali. Suppose 1 mgr. of nitric acid (= 0.25 %) had been retained in that quantity it is sure to have dissolved together with the whole of the main product. 1 mgr. = 0.016 millimol. 1 cm.^{3} of the alkali corresponds with 0.1 millimol. so that 0.16 cm.^{3} or about 3 drops are required for neutralisation. As the molecular weight of chloronitrobenzoic acid is 201.5 and that of bromonitrobenzoic acid 246, 0.016 millimol. represents, respectively, a weight of 3.2 and 3.9 mgr. or of $^3/_4$ % and 1 % of the nitration mixture. The main product contained therein is therefore found too high and the byeproduct correspondingly too low since the latter is found by difference. As the content in byeproduct in these mixtures does not exceed 13 % (in the bromo-acids) an error of 1 % is a rather serious one.

In order to be able to determine the composition of the nitration mixtures by solubility determinations it was necessary to determine first for the chloro- and bromobenzoic acids, the solubility of the least soluble ones (in both cases the byeproduct) and then the total solubility, when the liquid is kept saturated with this least soluble acid, but mixed with gradually increasing portions of the main product; when the liquid does not get saturated, all the main product passes into solution. By means of the solubility tables thus obtained the composition of an unknown mixture may be deduced reversedly by determining its solubility figure.

SOLUBILITY LINES.

Temperature 25.°0.

1. *Bromonitrobenzoic acids*



MW 246

Quantity of substance shaken with 100 cc. of water	Pipetted off	cc. of alkali (0.0287 n)	Total solubility in grams per 100 cc. of solution
100 mgrs. α	59.455 grs.	2.75	0.033
1 gram β	60.180 „	63.15	0.741
100mgrs. α + 118.8mgrs. β	26.211 „	5.00	0.135
„ + 203.7 „ „	32.345 „	9.90	0.216
„ + 299.0 „ „	31.050 „	13.60	0.309
„ + 402.0 „ „	19.021 „	11.00	0.408
„ + 497.6 „ „	20.176 „	15.65	0.502
„ + 587.3 „ „	20.337 „	17.05	0.592

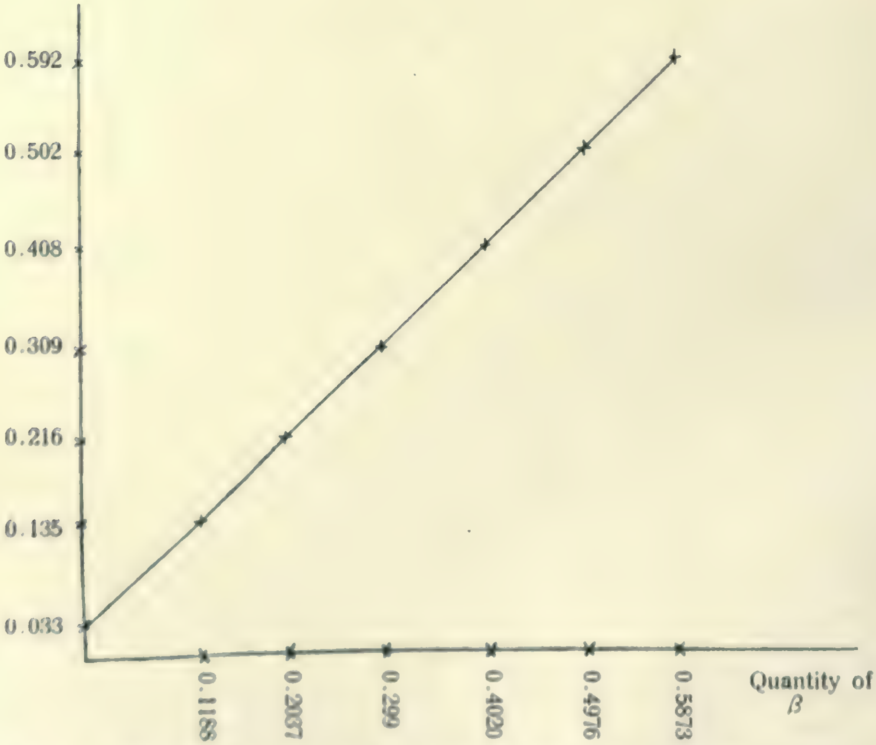
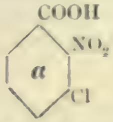


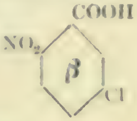
Fig. 1. Total solubility of mixtures of the bromonitrobenzoic acids constructed according to the table.

Duplicate determinations made by again titrating an aliquot portion from the bottles gave results within the limit of experimental error.

The graphic representation Fig. 1 shows that the line, except for a small deviation at the start, is a straight one.

2. *Chloronitrobenzoic acids.*





Temp. 25.°0 MW 201.5.

Quantity of substance shaken with 100 cc. of water	Pipetted off	cc. of alkali (0.0295 *n*)	Total solubility in grams per 100 cc. of solution
150 mgrs. α	37.611 grs.	3.0 cc.	0.047
1 gr. β	18.378 ,,	29.20	0.967
100 mgrs. α + 0.3020 β	29.650 ,,	15.70	0.315
100 mgrs. α + 0.4120 β	23.240 ,,	16.35	0.418

These titrations are accurate within 2 drops of 0.03 normal alkali. As this corresponds with about 0.7 mgr. of chloro- and 0.8 mgr. of bromonitrobenzoic acid the last figure of the numbers of the last column may be about one unit wrong. The tables have been constructed by Mr. Polak.

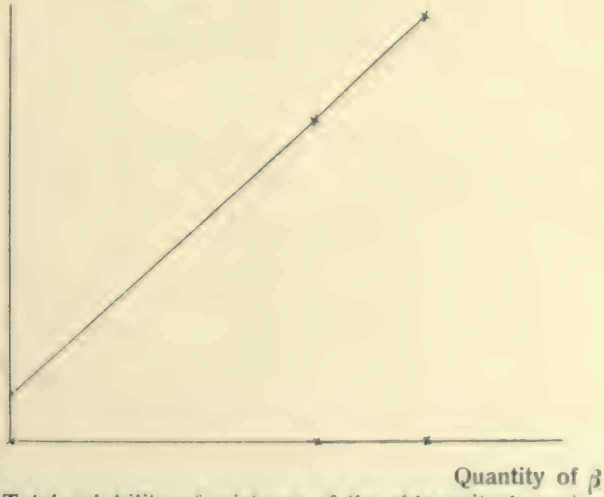


Fig. 2. Total solubility of mixtures of the chloronitrobenzoic acids, constructed according to the table.

As may be seen from fig. 2, the line is practically a straight one.

The nitrations of *m*-chloro- and *m*-bromobenzoic acid were carried out in the approved manner by means of absolute nitric acid at 0° and at —30°. In order to ascertain whether all had been converted into mononitro-acids the molecular weight of the products formed was determined by titration. For this purpose 0.1 gram of the nitration mixture was dissolved in water and titrated with N/10 alkali; when using phenolphthaleine as indicator this titration is accurate within one drop. 0.1 gram is about 0.5 millimol of chloro- and 0.4 millimol of bromonitrobenzoic acid which require 5 and 4 cc. of N/10 alkali respectively. One drop (0.05 cc.) corresponds therefore, with 1°/₀ of the molecular weight of the chloro- or 0.8°/₀ of the bromo-acid. If now the molecular weight lies between 201.5 ± 2 or 246 ± 2, respectively the substance may be taken to be pure nitro-acid. True it might be possible that, accidentally, a mixture had formed consisting of unattacked acid, mononitro- aud dinitro-acid, which apparently possesses the molecular weight of the pure mononitro-acid but apart from the improbability that this should have formed, the possibility was also excluded, because the nitration mixture of *m*-bromobenzoic acid was again treated with absolute nitric-acid, which caused no serious alteration in the molecular weight. Mol. weight first 245; on repeated treatment 247.

Mr. De Leeuw obtained the following results in the analysis of the nitration products prepared by himself.

I. Nitration of *m*-chlorobenzoic acid at 0°; 5 grams treated with 30 grams of absolute nitric acid.

Mol. weight of the product 203.2.

1. Weighed 381.9 mgrs. of nitration product; shaken with about 100 mgrs. of byeproduct ($CO_2H, Cl, NO_2 = 1, 3, 2$) and 100 grams of water at 25°.0.

Pipetted off 36.256 grams of solution which required 15.10 cc. of 0.0432 normal potassium hydroxide for neutralisation.

Main product 92.4°/₀; byeproduct 7.6°/₀.

2. Weighed 364.1 mgrs. of nitration product; shaken with about 100 mgrs. of byeproduct and 100 grams of water at 25°.0.

Pipetted off 69.464 grams which required 27.85 cc. of the said alkali for neutralisation.

Main product 92.8°/₀; byeproduct 7.2°/₀.

II. Nitration of *m*-chlorobenzoic acid at —30°; 5 grams treated with 30 grams of absolute nitric acid.

Molecular weight of the nitration product 200.4.

1. Weighed 351.7 mgrs. of the product; shaken with about 100 mgrs. of byeproduct and 100 grams of water at 25°. Pipetted off 34.538 grams of solution which required 13.5 cc. of the above alkali for neutralisation.

Main product 93.5°/₀; byeproduct 6.5°/₀.

2. 372.8 mgrs. treated as directed; Pipetted off 35.448 grams of solution which required 14.51 cc. of alkali for neutralisation.

Main product 92.8%; byeproduct 7.2%.

III. Nitration of *m*-bromobenzoic acid at 0°.

5 grams treated with 30 grams of absolute nitric acid.

Mol. weight of the nitration product 243.7.

Weighed 424.0 mgrs. of the product; shaken with 100 mgrs. of byeproduct and 100 grams of water at 25°. Pipetted off 33.945 grams which required 12.19 cc. of alkali for neutralisation.

Main product 88.3%; byeproduct 11.7%.

IV. Nitration of *m*-bromobenzoic acid at —30°.

Mol. weight 243.4.

374.4 mgrs. treated as directed. Pipetted off 31.661 grams of liquid which required 9.91 cc. of alkali for neutralisition.

Main product 88.6%; byeproduct 11.4%.

Mr. Polak has repeated these investigations with great care in which he used material prepared by himself. In order to be sure that the nitration products did not retain any nitric acid they were analysed in the manner described, after the test with diphenylamine had become negative. The remainder of the preparation was then again triturated and washed with cold water; the dissolved organic acids were recovered from the washings and the preparation thus purified was again submitted to analysis. The two analyses are indicated with I and II.

Cl 0°. M.W. 202,9 (201,5).

I	0,3374 gr. of nit. mixture +100 mgr. of α in 100 cc.	94.333 gr. of sol. β 0.3104	16.39 cc. of (0.0922) *n* alkali β **92.9%**	Tot. sol. 0.328 α **8.0%**
II	0,3315 gr. of nit. mixture +100 mgr. of α in 100 cc.	45.516 gr. of sol. β 0.3053	7.28 cc. of (0.0922) *n* alkali β **92.1%**	Tot. sol. 0.3180 α = **7.9%**

Cl—30° M.W. 203.8 (201.5).

I	0.3410 gr. of nitr. mixture	98.157 gr. of sol. β : 0.3181	17.43 cc. of (0.0922) *n* alkali β = **93.3%**	Tot. sol. 0.3300 α : **6.7%**
II	0.3275 gr. of nitr. mixture	66.284 gr. of sol. β 0.3068	11.40 cc. of (0.0922) *n* alkali β = **93.7%**	Tot. sol. 0.3195 α : **6.3%**

Br 0° M.W. 245.7 (246).

I	0.3320 gr. of nitr. mixture	55.477 gr. of sol. β 0.2898	7.32 cc. of (0.0922) *n* alkali β = **87.0%**	Tot. sol. 0.2993 α : **13.0%**
II	0 3292 gr. of nitr. mixture	67.915 gr. of sol. β 0.2868	8.96 cc. of (0.0922) *n* alkali β = **87.1%**	Tot. sol. 0.2971 α = **12.9%**

Br. —30°. M.W. 245.2 (246).

I	0.4585 gr. of nitr. mixture	89.965 gr. of sol. β = 0.4096	16.48 cc. of (0.0922) *n* alkali β : **89.3%**	Tot. sol. 0.4155 α : **10.7%**
II	0.4385 gr. of nitr. mixture	64.190 gr. of sol. β : 0.3192	11.20 cc. of (0.0922) *n* alkali β : **89.2%**	Tot. sol. 0.3957 α : **10.8%**

Let us now include all the figures obtained in the subjoined tables.

I. Nitration of *m*-chlorobenzoic acid; % of byeproduct in the nitration mixture.

	DE LEEUW		POLAK		HOLLEMAN, *R.***20**,206		
	%	mol. weight	%	mol. weight	%	mol. weight	mol. weight
Temp. 0°.	7.6 7.2	203.2	8.0 7.9	202.9	8.7	202.5	calculated
Temp. −30°.	6.5 7.2	200.4	6.7 6.3	203.8	8.3	201.5	201.5

II. Nitration of *m*-bromobenzoic acid.

Temp. 0°.	11.7	243.7	13.0 12.9	245.7	11.4	245	mol. weight calculated
Temp.—30°.	11.4	243.4	10.7 10.8	245.2	11.8	243.2	246

My own figures were deduced from solidifying point determinations. As regards the titration figures of Messrs. DE LEEUW and POLAK it must be observed that the end reaction was obtained within one drop of $n/10$ alkali so that there can be only a doubt as to one drop more or less. This represents $^1/_{200}$ millimol. or about 0.3 % of the quantity taken for analysis. If we consider further that the above figures are deduced from the tables communicated above, the figures of which present inaccuracies of the same order, the difference between the above percentages may be about 0.6 without exceeding the errors inherent to the process.

From this point of view Mr. POLAK's figures may be pronounced excellent ones. It appears from the table that when the molecular weights found approach more closely to the calculated ones, the percentage of the byeproducts is higher. This is easy of explanation. For the nitration product may be considered all the purer when there exists a closer agreement between the calculated molecular weight and that actually found. As, however, the impurities are dissolved on shaking with water, and count as main product in the titration, the figures of this become too high and those of the byeproducts consequently too low.

For this reason the following percentages, showing the composition of the nitration products, must be considered as being nearest to the truth.

I. Nitration of *m*-chlorobenzoic acid

	byeprod.	mean prod
Temp. 0°.	8	92
Temp.—30°.	7	93

II. Nitration of *m*-bromobenzoic acid

	byeprod.	main prod.
Temp. 0°.	13	87
Temp.—30°.	11	89

The uncertainty of the figures obtained from the solidifying point determinations is a little greater, owing to the circumstance that the mass darkens during the fusion, which causes the solidifying points (which are rather high) to be determined with less sharpness than is usually the case.

August 1908. *Amsterdam, Org. chem lab. University.*

Botany. — "*Contribution to the knowledge of the cytological development of Oenothera Lamarckiana*", by Mr. J. M. Geerts. (Communicated by Prof. F. A. F. C. Went).

(Communicated in the meeting of September 26, 1908).

Among the numerous plants, of which the cytological development has not yet been investigated, *Oenothera Lamarckiana* was the one selected, because a cytological examination of this plant would probably be of importance for the solution of other and more general questions.

Thus it may afterwards perhaps be possible, through a knowledge of the cytology of *Oenothera Lamarckiana* and its mutants, to find an explanation of mutation.

Although the mutation-theory has gained acceptance in most countries, this has not hitherto been the case in England to any considerable extent. There, Bateson and his pupils regard *Oen. Lam.* as a hybrid and attribute the origin of new species to hybrid segregation. The cheef argument in favour of this view is that *Oen. Lam.*, like many hybrids, shows a large degree of sterility in the ovules and pollen grains.

In this investigation I therefore set out to trace when and how this sterility arises, in order to be able to judge of the value of Bateson's argument.

It is quite conceivable that some day we may obtain a full insight into the conditions, through which mutations arise, and also that we may be able to bring about these conditions at will. For this purpose experiments with *Oen. Lam.* are especially desirable, in which attempts should be made to influence the origin of the mutants by subjecting the flowers to various conditions, for instance of temperature, or to various conditions of humidity, to injections etc.

In order to obtain reliable results in such experiments, it is necessary to know exactly, not only which flowers have been subjected to the influence, but also, in which developmental stage the flowers were at the time of treatment, whether before the synapsis, before or after the reducing division etc.; for then only can we determine whether a change in the number of mutants is really the result of the treatment, or is produced by other, unknown causes.

In order to make this investigation available for such experimental investigations, I have therefore also followed out the development of the flower, so as to be able to refer the principal cytological conditions to externally visible stages.

With reference to the mutants and hybrids of *Oen. Lam.* many questions arise of which the answers may be of importance to cytology itself. Especially hybrids with *O. gigas*, which mutant probably possesses twice as many chromosomes as *Oen. Lam.* itself, might provide material for interesting cytological investigations. For this purpose a knowledge of cytological development of the mutating plant itself is, however, a first desideratum.

The principal results obtained in this investigation, will now be briefly stated.

The floral development of *Oenothera Lamarckiana* was investigated in 1895 by Pohl [1]; this author arrived at conclusions, differing widely from those obtained for other *Onagraceae*, for instance by Barcianu [2]) and by Payer [3]), for according to Pohl the development is not acropetal, as found by the other investigators. It has now been found, however, that *Oen. Lam.* like other *Onagraceae* has an acropetal development of the flower. In addition the chief points observed in this development, are:

1. The corollar stamen arises from the protuberance, which the corolla forms on its inside.
2. The ovary is the floral axis, which has become hollow. Only the stigmas develop as 4 separate protuberances, alternating with the calyx stamens.
3. The ovary becomes quadrilocular by the growing inwards of 4 parietal septa, which stand before the calyx stamens and fuse in the centre.
4. The axis does not grow further; there is no columella.
5. The placentae are differentiated from the edges of the septa.
6. A corollar stamen and its petal have no common vascular bundle.
7. The ovule arises from periblem and dermatogen, except for the vascular bundle in the raphe.

The cytological development was studied both in the ovules and in the stamens. A summary of the principal phenomena observed, is here appended.

When the mother-cells go into synapsis, the nuclear network contracts, and a thin thread arises, in which chromatin particles can be seen. This thread contracts to a tangle and continually becomes shorter and therefore thicker; this is clearly visible when the tangle unrolls itself again. The thick thread now divides transversely into 14 chromosomes, the nuclear wall disappears, and the chromosomes place themselves perpendicularly to the long axis of the spindle of the heterotypic division. *In the synapsis of Oen. Lam. no double thread can therefore be seen; from that thread the vegetative number of chromosomes is formed, and just before the division these chromosomes show pairing.*

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[1]) Ueber Variationsweite der *Oenothera Lamarckiana* von J. Pohl Oesterr. botan. Zeitschrift Jahrgang 1895 Nr. 5 u 6.

[2]) Untersuchungen ueber die Bluethenentwicklung der *Onagraceae*, Inaug. diss. von D. P. Barcianu, Naumburg 1874.

[3]) J. B. Payer, Organogénie de la Fleur.

Both in the ovules and in the stamens the synapsis takes place in this manner. In the first division of the mother-cells entire chromosomes separate, which already during this division show a longitudinal splitting for the second division. After this heterotypic division the two nuclei scarcely enter upon a stage of rest, the chromosomes, split longitudinally, always remain visible, especially in the mother-cells of the embryosac. The wall between the two nuclei is often not formed completely. At the second division the halves of the two chromosomes separate, so that 4 nuclei are formed; in general but little staining substance is visible [1]).

Whereas in most plants the lowest-cell of the tetrad grows out to form the definitive embryosac, this is not so in *Oen. Lam. Here the uppermost cell becomes the embryosac*, while the other three degenerate; the chromatin of these three cells quits the nucleus, of which the wall disappears, and the chromatin now colours the whole protoplasm dark, so that these three cells of the tetrad remain visible for a long time as a long dark band under the embryosac. In that cell of the tetrad, which grows out, three successive divisions take place in almost all plants, so that 8 nuclei are formed. In *Oenothera* I always found but 4 nuclei, which come to lie in the upper part of the embryosac. A limited number of nuclei is also known in *Helosis guyanensis*, in consequence of the researches of Chodat and Bernard [2]) and in *Mourera*, through an investigation of Went [3]). In these plants the lower of the two nuclei, which are formed in the first division, probably degenerates; from the upper nucleus the three nuclei of the egg-apparatus and the polar nucleus are formed so that division nevertheless takes place three times.

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[1]) In the May meeting of the Dutch Botanical Society, in which I dealt with the greater portion of this subject, I already stated that the synapsis in *Oen. Lam.* takes place in this manner, thereby differing from what has been stated to occur in other plants. As I found in the beginning of September there appeared in the July number of the Botanical Gazette a paper by Gates on the synapsis and reducing divisions in the pollen mother-cells of *Oenothera rubrinervis*. This observer gives much the same succession of stages for the synapsis of this plant.

[2]) R. Chodat et C. Bernard. Sur le sac embryonnaire de *l'Helosis guyanensis*. Journal de Botanique T. XIV, 1900 p. 72.

[3]) F. A. F. C. Went. "The development of the ovule embryo-sac and egg in *Podostemaceae*." Recueil des Travaux Botaniques Néerlandais, Volume V, Livraison I, 1908.

In *Oen. Lam.* I never found a nucleus or remains of a nucleus in the lower part of the embryosac, whilst the four nuclei always lie in the upper portion. A few times it was possible to observe the divisions themselves. Thus I found an embryosac, in which the nucleus was dividing into two, with its spindle in the long axis of the embryosac. Further I found embryosacs with two nuclei, which were sometimes superposed, sometimes side by side. Therefore the lower nucleus probably changes its place, coming to lie higher up in the embryosac. The divisions of these two cells were also found, namely two spindles, in the upper part of the embryosac, and at right angles to each other. In the same manner the spindles are found in most plants above and below in the embryosac, at the third division in couples perpendicular to each other. The division of these two nuclei in *Oen. Lam.* is therefore pretty certainly the last division of the embryosac, in which the two synergids are formed from one nucleus, and the egg-nucleus and the upper polar nucleus from the other. In this particular embryosac, with the two spindles at right angles to each other, there was moreover no trace of nuclei at the chalazal end. We may therefore assume, that in *Oen. Lam.* the first division in the embryosac is suppressed, so that antipodal cells and lower polar nucleus are not formed at all, and that there is not even an antipodal initial cell, which occasionally degenerates again after being formed, as in *Helosis* and *Mourera.*

In the embryo-sac of *Cypripedium* the number of the divisions is still further reduced; here, according to Miss L. PACE¹) there occurs in the embryosac only one homoiotypic division in the lower cell; the upper cell degenerates. The homoiotypic division is not followed by a cell-division. The two nuclei in the lower cell now arrange themselves at the poles; this cell grows out longitudinally and the nuclei divide again, so that they are four in number. Further divisions do not take place in the embryosac; the four nuclei become egg cell, synergids and upper polar nucleus.

When in *Oen. Lam.* the four nuclei have been formed the synergids, which lie nearest to the micropyle, surround themselves, like the egg-nucleus, with their own plasma; the upper polar nucleus remains free in the plasma of the embryosac.

The four cells, which have arisen in the pollen mother-cells through the reduction division, grow out regularly to pollen-grains; the method of origin and the structure of the walls probably agrees in

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¹) LULA PACE. Fertilization in Cypripedum. Botanical Gazette. XLIV. 1907 p. 353.

Oen. Lam. with what R. BEER[1]) has described for *Oenothera longiflora*.

When the pollen-grains are almost mature, the generative and the vegetative nucleus are formed by division; the generative nucleus, which is the smaller, and is surrounded by a quantity of plasma, then applies itself to the wall; the vegetative nucleus remains in the middle of the grain. The division of the generative nucleus into two probably takes place in the pollen-tube.

The pollen-tube penetrates through the micropyle and through the nucellar tissue. It seems as if in this place the nucellar tissue already becomes in advance disorganized. Since, when the pollen-tubes penetrate, the synergids are already completely disorganized and stain very deeply, and since in the nucellus, at the spot where the pollen-tube has penetrated, dark coloured remnants are everywhere visible, I have not succeeded in observing the division of the generative nucleus. Fertilisation itself was however clearly observed. A double fertilisation takes place; one nucleus penetrates into the egg-cell and applies itself against the nucleus; the generative nucleus is at that time round, but smaller than the egg-nucleus, although it probably becomes somewhat larger before fusion. The other generative nucleus, which presents the same shape, applies itself to the polar nucleus. The fusion between the polar nucleus and its generative nucleus takes place more rapidly than that of the other generative nucleus with the egg-nucleus. The fertilized polar nucleus now soon divides, so that frequently there are already a number of endosperm nuclei before the egg-nucleus has completely coalesced with the generative nucleus, and before the egg-cell has a wall of its own. The fertilized egg-cell grows out to a short suspensor, and an embryo with distinct octants. Endosperm nuclei then already lie along the whole of the wall of the embryosac. Afterwards this endosperm however again disappears.

In Oenothera Lamarckiana the endosperm is therefore formed from one fertilized polar nucleus.

In mature stamens very many sterile grains are found in the pollen; in young fruits there occur between the developing seeds a fairly large number of ovules, which are not undergoing development. In both cases the sterility arises after the reduction division. Whilst in all embryo-sac mother-cells the reduction division takes place normally, there are still many ovules in which the upper tetrad cell also degenerates, this degeneration being accompanied by much the same phenomena as occur regularly in the three lower cells of the tetrad. In the pollen mother-cells also the divisions take place regularly, but after 4 tetrad cells have been formed, only two cells, in general, develop properly, the other two only partially, so that from them grains are formed, from which the contents gradually disappear, although the wall is fairly normal in structure.

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[1]) On the development of the pollen grain and anther of some Onagraceae, RUDOLF BEER. Beih. zum Bot. Centr. blatt 1905, 19 I.

Since the divisions are normal, the appearance of this sterility need not at all be the result of a hybrid nature. It follows from the literature on sterility, that, besides in hybrids, sterility occurs in many other plants, and that in most hybrids, which have been examined cytologically, sterility was already present in one or both parents. And since an examination of one hundred species showed sterility to be pretty common among *Onagraceae*, we are not, in my opinion, justified in deducing from the sterility of a plant that it is a hybrid. If the above-mentioned objection of BATESON against the mutation-theory is to have value, it will be incumbent upon him to name the presumptive parents of *Oen. Lam.*

In mature ovaries those ovules, which are not destined to develop, may be recognized by their more transparent nucellus, not containing an embryosac. In such ovulus the penetration of a pollen-tube was never observed, whereas this was repeatedly found in the normal ovules of the same section. *It would appear, therefore, that the normal embryosac exerts an attraction on the pollen-tubes.*

By combining the results of the investigation of the ontogenetic, with those of the cytological development, it appears, that *Oen. Lam.* is very suitable for the experiments, referred to in the introduction, because the cytological development of the pollen and of the ovules are sharply separated in point of time. In flowers of 30 mm. the development of the pollen is almost complete, while in the same flowers the development of the mother-cells in the ovule is only beginning. It would therefore be possible to influence the pollen and the ovules separately, and the flowers which should be selected for this purpose, can be easily recognized after a little practice. Should one wish to influence the pollen before the synapsis, then flowers 10—11 m.m. long should be selected, in which the stamens have a length of 3 mm., since the synapsis of the pollen takes place in flowers of 12—13 mm., in which the anther and also the filament have a length of 4 mm. The synapsis of the embryosac mother-cell takes place in flowers of about 3½ cm. In order to influence this, flowers of 3—3½ cm. should therefore be selected, in which the ovary and the calyx tube have about the same length i.e. 4½ mm.

I hope soon to be able to publish a more detailed description, with plates, of the results of this investigation in the Recueil des Travaux Botaniques Néerlandais.

Physiology. — *"About the independence of the electrocardiogram with regard to the form-cardiogram."* By A. K. M. Noyons, assistant in the Physiol. Lab. at Utrecht. (Communicated by Prof. H. Zwaardemaker).

Principally by the investigations of Engelmann [1]) and Marchand [2]) the electromotive phenomena which show themselves in every contracting heart and which we now register in the electrocardiogram, have been reduced to manifestations of the changed current of action that can be produced in every muscular tissue by direct or indirect stimulation of the muscular elements.

Contraction being usually considered as the only visible manifestation of muscular stimulation and action, the electric phenomenon is involuntarily thought to be connected with the process of contraction. On theoretical grounds, however, Biedermann [3]) deemed it quite possible, "dasz eine Muskelstelle erregt ist und daher sich negativ zu benachbarten, ruhenden Stellen verhält, ohne dabei in merklichem Grade contrahirt zu sein." In these theoretical considerations lies the nucleus of my investigations. Now the experiment teaches that these conceptions are in accordance with reality.

Already in my dissertation [4]) I have, in consequence of some experiments, pronounced the supposition that the electric phenomenon in the contracting heart represents a process by itself, which is borne out by the following experiments.

The heart of an Anodonta fluviatilis, laid bare, is in its natural position by means of the unpolarizable magazine-electrodes conducted to the string-galvanometer. (The electrodes with their cottonseeds have previously been put in fresh water for a quarter of an hour and subsequently in the pericard-liquor of the mussel).

The string-galvanometer of Einthoven with permanent magnet (Edelmann's small model) is fed by a current of 4 volt with moderate string-tension (38 out of 60 dividing lines). The movements of the heart are registered by a little lever with a small fulcrum and by a bit of straw placed vertically on the axis, which throws a silhouette on the chink of the registrating apparatus. The registration takes place by means of photography.

As appears from the first half of fig. 1 the heart shows regular contractions, attended by electric oscillations, which begin a little earlier.

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[1]) Engelmann, Pflüger's Archiv, Bd. XVII, 1878.

[2]) Marchand, Pflüger's Archiv, Bd XVI 1877 and XVII 1878.

[3]) Biedermann W., Elektrophysiologie, Jena 1895, page 322.

[4]) Noyons A. K. M. Proefschrift: Over den autotonus der spieren, Utrecht 1908

The cross indicates the place where 3 gtt. of a 3°/$_0$ KCl-solution are dripped upon the heart, which after some time causes a stopping of the form-cardiogram, while the electric phenomenon is altered. Shortly after the KCl-application some feeble movements of the heart are still perceptible in the lever, but they soon stop, whilst the electric fluctuations, which in the beginning of the chemical stimulation-process had become slight, have now nearly reached their original size again.

In fig. 2 the stopping of the heart is seen, while the electrocardiogram remains.

With another trial-object (Anodonta fluviatilis), besides those described, also other peculiarities were observed. When by the action of the chemical materials the heart had stopped, the electric phenomenon with the usual frequency of the heart-contractions every time continued manifesting itself periodically. But besides this periodicity it was also clearly observed that in these rhythmic electric phenomena mutually other group-formations appeared, which possessed about the same duration as the periodic length-fluctuations of the autotonus, which, before the stopping of the form-cardiogram, had already been clearly perceptible also in the form-cardiogram.

Also with other animals I had an opportunity to collect data for the independence of the electrocardiogram of the form-cardiogram. The following experiment proves this beyond the possibility of doubt in the heart of Tripodonotus natrix under digitonine-poisoning. The heart of a ringed snake was prepared in the afternoon of May 29th. After laying it bare and tying off the veins, the heart was cut out and fixed upon a cork-plate, while the heart-basis and ventricle-point were conducted to the string-galvanometer as described above. The movements of the atrium and ventricle were registered according to suspension-method. Fig. 3 gives the photografic registration of the form-cardiogram and electrocardiogram in the unpoisoned heart.

That same afternoon 5 gtt. of 1°/$_0$ digitonine dissolved in 0.9°/$_0$ NaCl having been added to the heart, we see after some time the typical phenomena of the digitonine-intoxication appear. The next day the heart shows no more alterations in form, unless by means of some expedients (washing with 0.9°/$_0$ NaCl and dripping on of 5 gtt. of CaCl 1°/$_0$ and 3 gtt. of KCl 3°/$_0$). At 11.30 p m. the heart stands quite still. Notwithstanding this the electric phenomenon quietly continues rhythmically. This state lasts till May 31st. Constantly the electrocardiogram shows the usual spontaneous rhythm. Now 1°/$_0$ digitonine is anew and abundantly dripped upon the heart, which causes a marked effect upon the electric phenomenon. This effect resembles in its form wellnigh exactly the electric alterations of the electrocardiogram, which already some days before were brought about by dripping the same material upon the heart. See fig. 4.

That the deviation of the string under the influence of the poisoning with digitonine is not a consequence of mechanical or chemical changes in the contact-places of the electrodes, was taught me by repeatedly dripping the electrodes, when the heart was quite dead, while the stringdeviation did not take place.

All through that day the regular, periodical electric fluctuations continue though they constantly diminish in size.

It appears that by radiating heat or by cooling down, the frequency and the size of these fluctuations can be respectively increased and decreased, without anything suggesting change of form in the heart being observed. On June 1st the heart stands completely still, also in an electric respect. It only appears that in communication with the galvanometer the heart shows for the first time a strong demarcation-current, proving that it is now partly dead.

Also with a frog's heart I often had an opportunity to observe that the eletrocardiogram remains observable after digitalis-intoxication, while the heart shows no change of form. Nor may for this remaining eletrocardiogram "fibrillaire Zuckungen", as muscular action, be held responsible, because also when observed with a strong magnifying glass, these movements did not appear visible, while nevertheless the heart quietly continued pulsating electrically.

This peculiar state under digitalis-intoxication is reached best and most certainly, if the heart is not poisoned by administering a larger dose at one time, but by repeatedly dripping new small doses during the whole process of poisoning. In this way I once succeeded in calling forth at a stoppage of the changes of form an electric phenomenon, which for a long time remained larger than the normal electrocardiogram before the poisoning.

If in this way, the poisoning fractioned, takes place with small doses, it may occur that the initial diminution of the electrocardiogram under the influence of the intoxication is at its appearance slackened to a considerable extent. On the whole the above mentioned digitalis intoxication-phenomena in the electrocardiogram may be brought about without differences worth mentioning, both by applying digitaleine and digitonine.

Of one of these poisoning-experiments there follows here a short account. In a Rana temporaria, of which cerebrum and spinal marrow have been destroyed by a piqure, atrium and ventricle are suspended according to the suspension-method, and basis and apex cordis are conducted by means of unpolarizable electrodes to the string-galvanometer with permanent magnet. The string-galvanometer is fed with 4 volt.; the string-tension is considerable and amounts to 7 out of the 60 lines of division.

The heart pulsates quietly and vigorously. Some seconds after the beginning of the registration 3 gutturae of a 1 $^0/_0$ solution of digitaleine in 0.9 $^0/_0$ Na Cl are dripped on the heart. At once the heart begins to react on this with a slight acceleration in its pulsation whilst the tonus of atrium and ventricle decrease, but shortly after increase considerably. The electrocardiogram, first becoming smaller, soon increases considerably in size, while the rest-position of the string in the interval of the heart-contraction moves to one side. This is shown by fig. 5. Every second minute the dripping with digitaleine is repeated, without every time causing anew the electric changes mentioned. Gradually the contractions of atrium and ventricle grow smaller, whilst the tonus of both increases considerably. A quarter of an hour after the first poisoning the heart stands completely still in systole, as appears from the registration and from the examination of the heart. The electrocardiogram quietly continues pulsating and shows large and small interchanging fluctuations, as is seen in fig. 6. After the lapse of five minutes also the electrocardic pulsations grow smaller and half an hour after the first poisoning they have entirely stopped. Also Fano and Fayod[1]) make mention of electric changes in the heart of Emys, stopping under digitalis-poisoning.

Finally we may mention as a proof for the independence of the electrocardiogram the total discongruity between the electric phenomenon and the form-cardiogram, as it appears in the treatment of the heart only, or of the whole trial-animal with toxic materials, though it be in this case impossible to bring about a complete rest of atrium and ventricle. Similar discongruities show themselves e. g. in dripping the heart with antiarine, nitras strychnini, sulfas atropini; by injecting nitras strychnini, sulfas atropini and coffeïnum into the veins of the trial-animal; further by exposing the animal in toto to vapours of chloroform, ether and acetic acid.

It is not only the whole heart that shows these discongruities and the peculiar, more or less typical reactions on the applied materials, but also separate parts of the heart may offer such phenomena, as appeared to me when examining the cut-out ventricle of the heart of an eel under the application of antiarine and digitaleïne.

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[1]) Fano et Fayod. De quelques rapports entre les propriétés électriques des oreilettes du coeur. Archiv. ital. de Biologie Tome IX 1888.

From what is said above we may conclude not only that in the spontaneously pulsating heart there appear still other actions than those which we find expressed in the contraction, but also that these actions are to some extent independent. The actions not visible to the eye and characterized by definite electric phenomena, suggest the results of stimulation-processes as they can be shown also in the nerve without accompanying change of form. Though, however, the electrocardiogram may possess a certain independence of the form-cardiogram, the above communication does not in the least afford a reason to conversely come to the conclusion of the independence of the latter with respect to the former.

Mathematics. — "*On groups of polyhedra with diagonal planes, derived from polytopes*". By Prof. P. H. Schoute.

Introduction.

1. By "diagonal plane" of a polyhedron we understand any plane having only edges in common with the boundary of that body.[1])

There are two regular polyhedra admitting diagonal planes, the octahedron and the icosahedron. Through any edge of the octahedron passes one diagonal plane, containing the centre and bisecting the dihedral angle of the two faces passing through the edge. Through any edge of the icosahedron pass two diagonal planes; the angle formed by these planes and that formed by the two faces through the edge have the bisecting planes in common, and the cross-ratio between the couple of diagonal planes and the couple of faces has $\frac{1}{2}(3-\sqrt{5})$ for one of its six mutually connected values.

The fact that only the two mentioned regular bodies possess diagonal planes is closely connected with this that through each of the vertices pass more than three faces. If we take away from the triangular faces meeting in a vertex the sides passing through that vertex, so as to retain of each the side opposite to this vertex, we find in the case of the octahedron a square adjacent to this vertex, in the case of the icosahedron a regular pentagon adjacent to this vertex, situated in a diagonal plane. Through any edge AB of the icosahedron pass two diagonal planes, as AB lies in two faces ABP and ABQ and therefore also in the diagonal planes corresponding to P, Q. Through any edge AB of the octahedron passes only one diagonal plane, as the third vertices P, Q of the faces ABP, ABQ through AB are opposite vertices and those points lead here to the same diagonal plane.

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[1]) In the last memoir of Dr. Fr. Schuh with the title "Over de meetkundige plaats, etc." (On the locus of the points in the plane, the sum of the distances of which to n given straight lines is constant, and analogous problems in space of three and more dimensions, Verhandelingen Kon. Akademie Amsterdam, first section volume IX, no. 5, 1908) occurs a series of polyhedra with the property that through any edge passes one diagonal plane. By extension to polydimensional spaces polytopes with diagonal spaces also make their appearance.

The diagonal planes of the icosahedron include a regular dodecahedron.

2. By "diagonal space" of a fourdimensional polytope we understand any space having only faces in common with the boundary of that polytope.

There are two regular cells admitting diagonal spaces, the C_{16} and the C_{600}. Through any face of the C_{16} passes one diagonal space, containing the centre and bisecting the dispatial angle of the two limiting bodies passing through the face. Through any face of the C_{600} pass two diagonal spaces; the angle formed by these spaces and that formed by the two limiting spaces through the face have the bisecting spaces in common, and the cross-ratio between the couple of diagonal spaces and the couple of limiting spaces has again — as we will prove afterwards — $\frac{1}{2}(3-\sqrt{5})$ for one of its six mutually connected values.

The fact that only the two mentioned regular cells possess diagonal spaces is again closely connected with this that through each of the vertices pass more than four limiting spaces and — we are obliged to add here — that these limiting spaces are tetrahedra [1]. If we take away from the limiting tetrahedra meeting in a vertex the faces passing through that vertex, so as to retain of each the face opposite to this vertex, we find in the case of the C_{16} a regular octahedron adjacent to this vertex, in the case of the C_{600} a regular icosahedron adjacent to this vertex, situated in a diagonal space. Through any face ABC of the C_{600} pass two diagonal spaces, as ABC lies in two spaces $ABCP$, $ABCQ$ and therefore also in the diagonal spaces corresponding to P, Q. Through any face ABC of the C_{16} passes only one diagonal space, as the fourth vertices P, Q of the limiting spaces $ABCP$, $ABCQ$ through ABC are opposite vertices and these points lead here to the same diagonal space.

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[1] This addition is necessary here. For the spatial sections of the regular C_{24} do not admit diagonal planes, though any vertex of this cell is situated in *six* of its limiting octahedra. As Mrs. A. BOOLE-STOTT pointed out to me these spatial sections admit what we may call "would-be diagonal planes." If we consider — see fig. 64 of vol II of my "*Mehrdimensionale Geometrie*" — of the six octahedra meeting in A the squares adjacent to A, we get the six faces of a cube, the vertices and the edges of which are vertices and edges of C_{24}, whilst the faces of it are not faces of C_{24}. If C_{24} is cut by a space intersecting this cube, the vertices of the section which are points of intersection with edges of the cube will lie in a plane without all the sides of the polygon of intersection with these points as vertices being edges of the section. In the fourth part of my communication "On fourdimensional nets and their sections by spaces" I hope to be able to come back to this point.

The diagonal spaces of the C_{600} include a regular C_{120}.

3. By "diagonal space Sp_{n-1}" of an n-dimensional polytope we understand any space Sp_{n-1} having with the boundary of this polytope only limiting spaces Sp_{n-2} in common.

Of the three regular polytopes, the simplex $S_{(n+1)}$ with $n+1$ vertices and $n+1$ limiting spaces Sp_{n-1}, the measure polytope M_n with 2^n vertices and $2n$ limiting spaces Sp_{n-1}, and the cross polytope Cr_n with reversely $2n$ vertices and 2^n limiting spaces Sp_{n-1}, only the last one possesses diagonal spaces Sp_{n-1}. Through any space Sp_{n-2} bearing a limiting simplex $S_{(n-1)}$ passes one diagonal space Sp_{n-1}, containing the centre and bisecting the angle between the two limiting spaces Sp_{n-1} passing through this Sp_{n-2}.

The fact that of the three regular polytopes only the cross polytope possesses diagonal spaces Sp_{n-1} is once more closely connected with this that through each of the vertices pass 2^{n-1} — and therefore more than n — limiting spaces Sp_{n-1}. If we take away from the limiting simplexes $S_{(n)}$ passing through any vertex the spaces Sp_{n-2} passing through this vertex, so as to retain the 2^{n-2} spaces Sp_{n-2} opposite to this vertex, we find the cross polytope Cr_{n-1} adjacent to this vertex, situated in a diagonal space Sp_{n-1}. Here too through any space Sp_{n-2} containing a limiting simplex $S_{(n-1)}$ pass two limiting spaces Sp_{n-1}. But, as the new vertices P and Q of the simplexes $S_{(n)}$ situated in these limiting spaces are opposite vertices of Cr_n leading to the same Cr_{n-1}, through each limiting simplex $S_{(n-1)}$ passes only one diagonal space Sp_{n-1}.

4. By intersecting a fourdimensional polytope, each face of which is situated in d diagonal spaces, by a space not containing an edge of the polytope, we get as section a polyhedron with the property that each of its edges is contained in d diagonal planes. For, if the intersecting space meets a face of the polytope, it meets also the d diagonal spaces passing through that face, and this always furnishes an edge of the section and d diagonal planes passing through it. So

the sections of the cells C_{16} and C_{600} by an arbitrarily chosen space are polyhedra with the property that through each edge passes respectively one diagonal plane or a couple of these. As four spaces passing in Sp_4 through the same face are cut by any space of Sp_4 in four planes through a line with the same cross-ratio, the sections of C_{600} by a space not containing an edge will be characterized by the property that the couples of faces and diagonal planes through an edge possess a constant cross-ratio. For from the regularity of C_{600} can be deduced that this cross-ratio is the same for all the faces, as we have stated already. Now the section of C_{600} by a space normal to an axis OE_0 (through a vertex E_0) is a regular icosahedron, if only the intersecting space is quite close to E_0 and this proves that the constant cross-ratio of C_{600} must be equal to that of the icosahedron.

5. Indeed, it is not difficult to show directly that the cross-ratio of C_{600} is really $\frac{1}{2}(3-\sqrt{5})$.

Let ABC be any face of C_{600} and O, P, Q (fig. 1) represent successively the centre of C_{600} and the fourth vertices of the two limiting tetrahedra $ABCP$, $ABCQ$ passing through ABC. Then the plane OPQ of the diagram will contain the centre of gravity G of the face ABC and be perfectly normal to this face in this point. From $GP=GQ$ and $OP=OQ$ can be deduced that the quadrangle $OPGQ$ is a deltoid with OG as axis of symmetry. As furthermore the normals GP' and GQ' dropped from G on OP and OQ are the traces of the plane of the diagram with the two diagonal spaces, we get for the cross-ratio $(PQRS)$

$$\frac{PR}{PS} : \frac{QR}{QS} = \left(\frac{PR}{PS}\right)^2 = \left(\frac{\tan\alpha - \tan\beta}{\tan\alpha + \tan\beta}\right)^2 = \frac{\sin^2(\alpha-\beta)}{\sin^2(\alpha+\beta)}.$$

Now if the edge of C_{600} is our unit and we represent for brevity's sake $\sqrt{5}$ by e we have (see my "*Mehrdimensionale Geometrie*", vol. II, p. 200)

$$OP = \frac{1}{2}(e+1),\ OP' = \frac{1}{4}(e+3),\ OG = \frac{1}{6}(e+3)\sqrt{3},\ PG = \frac{1}{3}\sqrt{6}.$$

From this ensues

$$\beta = 60^\circ,\ \sin\alpha = \frac{1}{8}(e+1)\sqrt{6},\ \cos\alpha = \frac{1}{4}\sqrt{7-3e}$$

and therefore

$$(PQRS) = \left(\frac{e-1}{2}\right)^2 = \frac{1}{2}(3-e) = 0{,}381966\ldots\ ^{1)}$$

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[1] In the same way the cross-ratio of the four planes through an edge of the icosahedron can be found.

6. In the third part of my communications "On fourdimensional nets and their sections by spaces", which is about to appear in these "Proceedings" we shall find occasion to fix attention on the diagonal planes presenting themselves in the sections of the C_{16}. As any vertex — or rather any couple of opposite vertices — of C_{16} possesses an adjacent octahedron, the polygons situated in these diagonal planes are always sections of octahedra. Probably the diagonal planes presenting themselves in the sections of the C_{600} were discovered for the first time by Mrs. A. BOOLE-STOTT, who made models of these sections, and explained as sections with diagonal spaces by Mr. H. W. CURJEL.[1])

The object of this paper is to study more closely the cases in which the intersecting space contains one or more edges of C_{16} and C_{600}; of the results revealed by these considerations these about C_{600} have especially roused our interest.

A. *The spatial sections through an edge of* C_{16}.

7. We consider the case in which the intersecting space contains the edge AB of C_{16} and indicate by A' and B' the vertices opposite to A and B. Then all the vertices except A and A' are adjacent to A and A', all the vertices except B and B' are adjacent to B and B', and so the four other vertices P_1, P_2, P_3, P_4 (fig. 2) are adjacent to A and B at the same time. In other words: the octahedra adjacent to A and B, situated in different spaces, penetrate one another in the square $P_1P_2P_3P_4$, the vertices of which they have in common. So through the edge AB pass two diagonal spaces, one of which corresponds to the opposite vertices P_1, P_3, the other to the opposite vertices P_2, P_4; they intersect the plane of the square $P_1P_2P_3P_4$, perfectly normal in O to the plane through AB and $A'B'$, respectively in the diagonals P_2P_4, P_1P_3. If l is the trace of the intersecting space through AB on the plane $P_1P_2P_3P_4$, and this line l, determining with AB that space, meets the diagonals P_2P_4, P_1P_3 in the points S_{13}, S_{24} situated within the square, then the section will show the particularity that the planes ABS_{13} and ABS_{24} are diagonal planes; so in some cases the edge AB will lie in *two* diagonal planes.

In the third communication "On fourdimensional nets, etc." quoted above will be indicated that the particularity of an edge being situated in two diagonal planes does not present itself in the four groups of principal sections of C_{16}.

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[1]) A series of these models, showing e.g. the decomposition of the 120 vertices of the C_{600} into the vertices of five cells C_{24}, has been inserted lately into the collection of mathematical models of the University of Groningen.

B. *The spatial sections through an edge of C_{600}.*

8. Through any edge AB (fig. 3) of C_{600} pass five limiting tetrahedra of this cell; the five edges opposite to AB of these tetrahedra are the sides of a regular pentagon $P_1P_2 \ldots P_5$, the vertices of which are at the same time adjacent to A and B. In other words: the icosahedra adjacent to A and B, situated in different spaces, penetrate one another in the regular pentagon $P_1P_2 \ldots P_5$, adjacent to AB, the vertices of which are common to both. So through the edge AB pass five diagonal spaces corresponding respectively to the five vertices $P_1, P_2, \ldots, P_5$; they intersect the plane of the pentagon, perfectly normal in its centre M to the plane ABM, in the diagonals P_5P_2, $P_1P_3, \ldots P_4P_1$ of the pentagon, or — if one likes — in the sides of the starpentagon $P_1P_3P_5P_2P_4$. In the case of C_{16} the centre O of the square $P_1P_2P_3P_4$ was at the same time the centre of the cell. Here the centre M of the pentagon is not even the centre of the two icosahedra penetrating one another, and still less the centre of C_{600}; here the line joining M to the midpoint M' of the edge AB must contain the centre O of C_{600}.

If the trace l of the intersecting space on the plane of the pentagon adjacent to AB cuts P_5P_2 in S_1 (fig. 3), ABS_1 is a diagonal plane. For this plane is the intersection of the intersecting space determined by AB and l with the diagonal space determined by AB and P_5P_2 of the icosahedron adjacent to P_1, and S_1 lies on P_5P_2 itself, not on its production. Indeed it is evident that this icosahedron is cut by any plane through AB and a point of P_5P_2, if this point lies on P_5P_2 itself, whilst the plane will contain of this icosahedron the edge AB only, if this point lies on P_5P_2 produced. In order to prove this we have only to observe that the lines AB and P_5P_2, the first of which is an edge of C_{600} and the latter a chord, cross one another normally. From this it ensues that these lines, likewise edge and chord of the icosahedron determined by the points A, B, P_5, P_2, can be represented (fig. 4), in projection on a plane through two opposite edges $pr, p'r'$ of the icosahedron, by the edge in q normal to the plane of the diagram and the chord pp' situated in that plane, the extremities of the edge being joined by edges to the extremities p, p' of that chord. This shows immediately that any plane through the edge projecting itself in q cuts the icosahedron or not, according to whether the point of intersection of the plane with pp' lies on this line itself or on its production.

So for the position of the intersecting space adopted in fig. 3 four diagonal planes ABS_1, ABS_2, ABS_3, ABS_4 pass through AB; the point of intersection S_5 of l and P_4P_1 falls on the production of this side and does not lead to a diagonal plane.

On each side P_5P_2 of the starpentagon (fig. 3) there are remarkable points besides the extremities P_5, P_2, which lead to faces and not to diagonal planes, namely the points of intersection Q_3, Q_1 with the other sides and the midpoint M_1. If S_1 coincides with Q_3, the sides P_5P_2 and P_4P_1 are cut in the same point and, the two corresponding diagonal planes coinciding with one another in the plane of intersection of the diagonal spaces ABP_5P_2 and ABP_4P_1 adjacent to P_1 and P_4, this plane must contain the pentagon adjacent to the edge P_1P_5 of C_{600}. So in this case the polygon situated in the diagonal plane — compare in fig. 4 the planes normal to the plane of the diagram in the lines qr and qr' — is a regular pentagon. If S_1 coincides with M_1 the plane ABM — compare fig. 4 —, being a plane of symmetry of the icosahedron, contains AB and the edge parallel to AB.

9. My second memoir with the title "Regelmässige Schnitte u.s.w." Regular sections and projections of C_{120} and C_{600}. Verhandelingen Amsterdam, first section, vol. IX, N°. 4, 1907 contains the data that enable us to determine, for any position of the intersecting space containing a certain number of edges of C_{600} belonging to the four groups of sections studied there, the number and the position of the diagonal planes passing through any one of these edges, and to construct the icosahedral sections situated in these planes. We will try to explain this shortly.

On the righthand side of the plates II, IV, VI, VIII has been indicated how the icosahedra adjacent to the vertices of C_{600} project themselves on the axes OR_0, OF_0, OK_0, OE_0. In order to see at a glance which sections normal to these axes do contain edges of icosahedra — and therefore also of C_{600} — we consult the upper lines of the plates XVIII, XVI, XIV, XII. We find then the following table:

II^b, XVIII	$a_1(6)$, $d_1(12)$, $e_1(12)$, $f_1(6)$,
IV^b, XVI	$a_2(3)$, $c_2(3)$, $e_2(3)$, $f_2(6)$, $h_2(6)$, $i_2(3)$,
VI^b, XIV	$a_3(1)$, $b_3(5)$, $c_3(10)$, $f_3(5)$, $g_3(10)$, $i_3(10)$,
VIII^b, XII	$b_4(30)$, $c_4(30)$, $e_4(60)$,

in which the indices 1, 2, 3, 4, distinguishing the groups, correspond to those of the groups of icosahedra on (II^b), IV^b, VI^b, $VIII^b$, whilst the numbers placed between brackets indicate how many edges lie in the intersecting spaces. However the cases a_1, a_2, a_3 can be left out, as referring to intersecting spaces leaving the C_{600} totally on one side and being therefore unable to furnish sections containing diagonal planes; for each of the sixteen remaining cases the trace l of the intersecting space on the plane of the pentagon adjacent to the chosen edge must be constructed. These traces, indicated by the symbols d_1, $e_1, \ldots, e_4$ of the cases to which they belong, are represented altogether in fig. 5.

10. The determination of the trace l causes the least trouble if this line contains two of the remarkable points P_i, Q_i, M_i corresponding respectively to a vertex, a point of intersection of two non-adjacent sides and the midpoint of a side of the starpentagon. In order to divide the difficulties we treat these simple cases first.

Case d_1. On plate II^b we find under d that the groups I and VII, each containing four icosahedra, furnish faces situated in the intersecting space, whilst group III gives six icosahedral sections through two opposite edges. So the trace d_1 to be found passes through a vertex P_i and a midpoint M_i; if P_1 is taken as P_i, then M_i must be either M_3 or M_4. So we find that the trace d_1 coincides with one out of ten homologous lines, if by "homologous" lines we mean lines passing into one another either by a rotation of the pentagon about its centre M to an amount of any multiple of 72° or by a reflexion with respect to one of the lines MP_i as mirror, i.e. in general by any transformation that transforms the pentagon into itself.

The line d_1 cuts two other sides, the sides P_5P_2 and P_3P_5, of the starpentagon; as P_1 does not lead to a diagonal plane, any of the 12 edges lying in the intersecting space is contained in three diagonal planes. These new diagonal planes are connected with the groups IV and VI, each of which contains 12 icosahedra. As the section passes rather near the centre M_i in the case of IV and rather near one of the extremities P_i in the case of VI, it is probable that IV corresponds to the point on P_5P_2, VI to the point on P_3P_5. Later on we will prove this to be true.

We will add the remark, that the number 12 of the edges lying in the intersecting space is given back by each of the groups I, III, IV, VI, VII, the corresponding diagonal planes — the *faces* of I and VII included — containing successively 3, 2, 1, 1, 3 edges.

Case e_3. On plate VI^b under e the group I_3 leads to a point Q

and the group II_3 to a point M_i; if Q_1 is chosen as Q_i, M_i must coincide either with M_2 or with M_5.

The chosen line c_3 furnishes one point of intersection more, on $P_5 P_2$; so there must be one group of icosahedra more with an edge situated in the intersecting space. Indeed, we find only one group VI_2, IV_8 belonging again to Q_1.

Case e_4. On plate VIII^b under e we have to deal with a central section of C'_{600}, from which ensues that the line e_4 passes through the centre M of the pentagon. Moreover the groups III_4, IV_4, V_4 furnish successively a point P_i, a point Q_i, a point M_i. So e_4 is a diameter through a vertex of the pentagon, e.g. $P_1 M_1 Q_1$. Here no other point of intersection appears.

11. It would be possible to go on in this manner and to treat successively, proceeding from the easier cases to the more difficult ones, the remaining lines through two remarkable points, the lines through only one remarkable point, the lines parallel to one of the sides. We prefer however to explain now, for an arbitrary case, how the ratio of division of the side of the starpentagon corresponding to a determined group of icosahedra can be found by means of Fig. 3 of the quoted memoir, which is repeated here with slight modification as fig. 4.

We therefore consider the group IV_1 of plate II^b mentioned above under d_1, and remember that the icosahedral sections corresponding to this group are determined, according to the quoted memoir, by planes normal to the plane of fig. 4 in a line parallel to pp^I. If the edge normal in q to the plane of that diagram is once more the edge AB and the chord pp' situated in that plane the side of the starpentagon, then the point S on that side determining the diagonal plane in question is found by drawing through q the line qS parallel to pp^I. Now pw is the smaller segment of the line pp' divided internally in medial section and the same relation holds for $p^{II}r = wq$ with respect to the segments $p^Ir = p^{II}s = sq$. So if the ratio of the side of the regular pentagon to its diagonal is indicated by $\frac{s}{d}$, we deduce from similar triangles

$$p^Iw : wq = pw : wS,$$

which may be transformed into

$$p^Iq : p^Iw = pS : pw\,.$$

This leads to

$$\frac{pS}{pp'} = \frac{3d+2s}{3d+s} \cdot \frac{pw}{pp'} = \frac{3d+2s}{3d+s} \quad \frac{d-s}{d} = \frac{(2+e)(3-e)}{5+e} = \frac{1+e}{e+5} = \frac{1}{5}\,e.$$

By this value the place of S on pp' is perfectly determined; however in fig. 5 we may — and, if d_1 has been determined by P_1 and M_3, we must — assume for S not the point on the right of M_1 corresponding to this ratio but the point on the left.

As a second example we consider the group IX$_2$ of plate VI^b to which — according to the second memoir — corresponds a series of planes normal to the plane of fig. 4 parallel to up_2^{III} (p_2^{III} being the midpoint of sv). We draw through s and q the lines sS'' and qS' parallel to up_2^{III} and determine now the ratio of pS' to pp' by means of similar triangles as follows. These triangles give

$$\frac{S'w'}{qw'}=\frac{w'S''}{w'w''}=\frac{pS''}{ps}=\frac{pS''}{w'u}=\frac{pw'}{w''u}=\frac{pw'}{\frac{1}{2}qu}.$$

So we have

$$\frac{S'w'}{pp'}=\frac{2qw'}{qu}\cdot\frac{pw'}{pp'}=\frac{2s}{d+s}\cdot\frac{s}{d}$$

and finally

$$\frac{pS'}{pp'}=\frac{pw'-S'w'}{pp'}=\frac{s}{d}\left(1-\frac{2s}{d+s}\right)=\frac{s\,(d-s)}{d\ \ d+s)}=\frac{(e-1)\,(3-e)}{2\,(e+1)}=\tfrac{1}{2}\,(7-3e)\,.$$

In this way is obtained the complete system of the twelve different ratios λ given in the following table, where, when λ differs from $\frac{1}{2}$, the value smaller than $\frac{1}{2}$ always appears. For all the groups in any horizontal row λ has the value indicated in the last column but one. In the last column are given the numbers of centimeters corresponding to these ratios, when the length of the side of the starpentagon (fig. 5) is 20 centimeters. Finally the last column but two indicates the direction of the trace of the intersecting planes normal to the plane of fig. 4, by means of which the values of λ have been calculated. (See table p. 287).

For the sake of clearness the values of λ with the side (20 centimeters) of the starpentagon of fig. 5 as unit have been indicated separately in fig. 6. By transferring this scale division in fig. 5 to each of the sides P_1P_2, etc. we are enabled to draw immediately each of the traces l in question with accuracy.

12. By means of the preceding the polygon of intersection of the polyhedron situated in any assigned diagonal plane can be constructed. To this end we indicate in fig. 7, which is a repetition of fig. 4, for the twelve different cases of the table by the numbers 1, 2, . . . , 12 the traces of the intersecting planes passing through the edge in q normal to the plane of the diagram, and show how we can obtain all the measures necessary for the construction of these

Nr.	Groups					λ	
1	I_1, II_1, VII_1	II_2, XI_2		III_4	qp	0	0
2	III_1	I_2, VII_2	II_3, V_3	V_4	qO	$\frac{1}{2}$	10
3			I_3, IV_3, $\overline{IX_3}$	II_4, IV_4	qs	$\frac{1}{2}(3-e)$	7.63932
4	IV_1		$VIII_3$		pp^{I}	$\frac{1}{5}e$	8.94427
5	V_1	IV_2			pp^{II}	$2(e-2)$	9.44272
6	VI_1		III_3		pp^{III}	$e-2$	4.72136
7	$VIII_1$	V_2			pp^{IV}	$\frac{1}{4}(e-1)$	6.18034
8		VI_2			pp_2^{II}	$\frac{1}{6}(5-e)$	9.14207
9		IX_2			up_2^{III}	$\frac{1}{2}(7-3e)$	2.91796
10		X_2	VI_3		qp_2^{IV}	$\frac{1}{10}(5-e)$	5.52786
11		XI_2			Op^{IV}	$\frac{1}{4}(3e-5)$	8.54102
12			IX_3		Or	$\frac{1}{4}(3-e)$	3.81966

polygons represented in fig. 8 by laying down in the plane of the diagram of fig. 7 the regular pentagon projecting itself in psr and the equilateral triangle projecting itself in rr. By the remark that all these polygons admit an axis of symmetry, the line k bisecting the edge $q_1 q_2$ normally, and that the measures qab, aa' of the pentagon of Nr. 9 and $qcde$, dd', ee' of the octogon of Nr. 4 used in fig. 8 are taken from fig. 7 this construction will become sufficiently clear.[1]

We add to this the following simple general remark. The polygon situated in a diagonal plane of which one of the sides is an edge of C_{600} is always either a pentagon, or a hexagon, or an octagon. If we once more determine the diagonal plane by means of the edge normal in q to the plane of fig. 4 and the point of intersection S with pp', then the section is a pentagon if S lies between p and

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[1] The letters a and c, that had to indicate points on k, have been omitted in fig. 8.

w or between w and p' and an octagon if S lies between w and w', except when S coincides with the midpoint in which case the section is a hexagon. In other words, with reference to the side $P_5 P_2$ of the starpentagon of fig. 5: the section is a hexagon if S coincides with M_1, an octagon if S lies elsewhere between Q_3 and Q_4, a pentagon if S falls between P_5 and Q_3 or Q_4 and P_2. So in the case h_2 we find two pentagons, since two points of intersection lie outside the pentagon with the vertices Q_i, a hexagon and an octogon, etc.

13. The method developed here has a slight drawback, revealing itself to the utmost in the determination of the exact position of the trace h_2. The difficulty consists in this that the method leaves us in the dark as to the succession of the different values of λ on the trace l. If we have deduced that the different ratios of VI$_2$, VII$_2$, IX$_2$, X$_2$ present themselves and we have chosen for VII$_2$ the centre M_2 (fig. 5) we are obliged to investigate by a rotation of the ruler about M_2 on which side — and in which of the two different points on this side — we must assume the point of division corresponding to VI$_2$ in order to make the other points of intersection to correspond to IX$_2$ and X$_2$. We now indicate finally how this difficulty can be overcome.

To any chosen edge of C_{600} projecting itself on plate IV^b in h on the axis OF_0, there correspond five adjacent points of C_{600}. If now it were possible:

1. to select a determined edge projecting itself in h on OF_0,

2. to point out the five adjacent vertices and to indicate in what order these points are the vertices of a regular starpentagon,

3. to find where these five points project themselves on the same axis OF_0,

then it would be possible to make out, in what ratio the successive sides of the starpentagon were divided in projection on OF_0 by h, which would enable us to fix in fig. 5 on each of these sides a quite definite point. Really in these suppositions the difficulty would be quite dissolved.

Now these suppositions are quite realisable, by means of the tables published in my first memoir with the title "Regelmässige Schnitte u. s. w." (Regular sections and projections of C_{120} and C_{600}, Verhandelingen Amsterdam, first section, vol. II, No. 7, 1894); we will explain this with the aid of fig. 9 for the case of the trace h_2.

14. In "Tabelle I" with the inscription "Coordinatenstellung des Z^{600}" we find, if under "C, Zweite Querlinie" the z_1 corresponds to the chosen axis OF_0, that the vertices

$$-6,\ 7,\ -11,\ -12,\ 17,\ -18,\ 19,\ 20,\ 33,\ -34,\ 35,\ 36$$

have $1+e$ for value of z_1 and project themselves therefore in h — compare plate IV^b of the second memoir. From "Tabelle II" with the inscription "Kanten des Z^{600}" we then deduce that (7,33) is an edge of C^{600}, that 14, 22, 25, 29, 51 are the five vertices adjacent to this edge (7,33) and these points form a regular pentagon $P_1P_2P_3P_4P_5$ in the order of succession 14, 22, 51, 29, 25 and therefore a regular starpentagon $P_1P_3P_5P_2P_4$ in the order 14, 51, 25, 22, 29. Turning back to the column z_1 of "Tabelle I" we find at last that these vertices 14, 51, 25, 22, 29 admit successively for z_1 the values

$$1-e,\ 4,\ 3+e,\ -2,\ 2\,(2+e),$$

from which ensues that they project themselves — compare again plate IV^b of the second memoir — in k', g, f, i', c. This result is indicated in fig. 9. While the segments of the horizontal lines appearing there from right to left are indicated as to their relative length by

$$d,\ s,\ d,\ d,\ s,\ d,\ s,\ d,\ d,\ s,$$

we find, if we indicate by S the point on any side of the starpentagon projecting itself in h,

$$\frac{P_3S}{P_3P_1} = \frac{s}{3d+2s} = \frac{1}{2}(7-3e), \qquad \frac{P_5S}{P_5P_2} = \frac{d+s}{4d+3s} = \frac{1}{10}(5-e)\,,$$

$$\frac{P_4S}{P_4P_2} = \frac{1}{2} \qquad , \qquad \frac{P_1S}{P_1P_4} = \frac{3d+s}{6d+3s} = \frac{1}{6}(5-e)\,.$$

These results are in accordance with what has been found before; moreover they indicate quite definitely the place of each point of division [1]).

15. If we apply the new method to the case of a trace as e_2 parallel to one of the sides of the starpentagon, then the point S projecting itself in e on plate IV^b will have to divide the side P_5P_2 externally into the ratio unity and this requires, as S does not lie at infinity, that the edge P_5P_2 projects itself on OF_0 as a point.

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[1]) As the second method gives something more in one respect than the first, it might seem superfluous to communicate the first. We are not of this opinion. For the first method has this advantage above the second that it leads immediately to a construction of the polygon situated in the diagonal plane as the section of a definite icosahedron by a definite plane.

This case is represented in fig. 10 for the edge (21, 24), where 3, 49, 50, 57, 58 are the five adjacent points, whilst 50, 3, 49, 57, 58 appears as the pentagon $P_1P_2P_3P_4P_5$, 50, 49, 58, 3, 57 as the starpentagon $P_1P_3P_5P_2P_4$. Really P_5P_2 projects itself into a point; moreover P_3P_1 and P_4P_1 on one hand and P_4P_2 and P_3P_5 on the other coincide in projection, which is closely connected with this that λ is the same for the two constituents of each pair.

Mathematics. — "*On triple systems, particularly those of thirteen elements.*" By Dr. J. A. BARRAU. (Communicated by Prof. D. J. KORTEWEG).

(Communicated in the meeting of September 26, 1908).

In a paper to this Academy [1]) Prof. J. DE VRIES gave a triple system of 13 elements of a different type than the cyclic system of Prof. NETTO [2]); he added however the observation, that no proof has been furnished of these types being the only ones.

Mr. K. ZULAUF shows in his dissertation [3]) that the systems given formerly by KIRKMAN (1853) and REISZ (1859) are identical to that of DE VRIES, so that the number of *known* systems is *two*; neither is anything here decided about the number of *possible* systems.

It seemed desirable to decide upon this point by means of a special investigation [4]). To this end some facility is offered by using those expressions which are used in the theory of the configurations, by regarding the 13 elements as *points*, the 26 triplets as *lines* which bear three of the points; the whole of the triple system then becomes the scheme of a diagonalless Cf. $(13_6, 26_3)$ where it is irrelevant whether this Cf. can be geometrically realized or not. A classification of these Cff. is now our aim in view.

The rest figure of the second order of a line of such a Cf., i.e. what remains if we leave out that line with its three points and the 3 × 5 lines passing through these points, is of necessity a Cf. (10_3), the 10 points of which are in three ways perspective and that according to the three points left out.

But then reversely each imaginable Cf. $(13_6, 26_3)$ of the desired type is obtained by:

1st. starting from all possible Cff. (10_3),

2nd. by constructing for each Cf. (10_3) the Cf. $(10_3, 15_2)$ of its diagonals,

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[1]) *Versl. Kon. Akad. v. Wet.* III, p. 64, 1894.

[2]) *Substitutionentheorie*, p. 220; *Math. Annalen*, Vol. 42.

[3]) "*Ueber Tripelsysteme von 13 Elementen*", Giessen, 1897.

[4]) I subsequently find this question treated also by DE PASQUALE (*Rendic. R. Ist. Lombardo*, 2nd Ser., 32, 1899).

3rd. by investigating for each of these Cff. $(10_3, 15_3)$ in how many ways its 15 lines break up into three *principal five-sides*[1]),

4th. by imagining for each of these cases the 5 lines of each principal five-side as converging to one point and these three points as collinear.

The number of types of Cff. (10_3) amounts, according to the classifications of Kantor[2]) and Schroeter[3]), to *ten*, to be distinguished

Those of the system of Kirkman are:

K	1	1	1	2	2	3	3	5	5	7	1	2	3	4	6	1	2	3	4	6	1	2	3	4	5	*a*
	2	4	6	4	8	4	9	6	7	8	8	5	7	0	9	9	0	5	7	8	0	7	6	9	8	*b*
	3	5	7	6	9	8	0	0	9	0	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
	IX	VIII	V	V	V	V	VIII	V	IX	V	VIII	V	V	II	VIII	VI	VIII	V	VIII	IX	X	III	III	X	III	X

The Cff. of the diagonals of the 10 Cff. (10_3) are resp.:

	II	III	IV	V	VI	VII	VIII	IX	X
1 8	1 8	1 8	1 8	1 8	1 8	1 8	1 8	1 8	1 8
1 9	1 9	1 9	1 9	1 9	1 9	1 9	1 9	1 9	1 9
1 0	1 0	1 0	1 0	1 0	1 0	1 0	1 0	1 0	1 0
2 5	2 5	2 5	2 6	2 6	2 5	2 5	2 5	2 5	2 5
2 7	2 7	2 6	2 7	2 7	2 7	2 7	2 9	2 6	2 7
2 0	2 0	2 0	2 0	2 0	2 0	2 0	2 0	2 4	2 9
3 4	3 4	3 4	3 4	3 4	3 4	3 4	3 5	3 7	3 5
3 6	3 6	3 7	3 5	3 5	3 6	3 6	3 6	3 8	3 6
3 0	3 0	3 0	3 0	3 9	3 9	3 8	3 7	3 0	3 7
4 7	4 7	4 7	4 7	4 7	4 7	4 7	4 7	4 7	4 7
4 9	4 9	4 9	4 9	4 0	4 9	4 9	4 8	4 9	4 8
5 6	5 6	5 6	5 6	5 6	5 6	5 6	4 9	5 6	4 9
5 9	5 8	5 8	5 8	5 8	5 8	5 0	5 7	5 0	5 0
6 8	6 8	6 9	6 9	6 8	6 8	6 8	6 8	6 8	6 8
7 8	7 9	7 8	7 8	7 9	7 0	7 9	6 0	7 9	6 0

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[1] By principal n-side of a Cf. Martinetti and de Vries understand a group of n Cf-lines which contain together once all the Cf-points.

[2] *Wiener Sitzungsberichte* 84, 1881.

[3] *Göttinger Nachrichten*, 1889, N°. 8.

1	1	1	1	8	2	3	2	3	4	5	1	2	3	5	7	1	2	4	3	6	1	2	3	4	5	*a*
	2	4	6	9	4	7	6	5	6	7	8	0	4	6	9	9	5	7	0	8	0	7	6	9	8	*b*
	3	5	7	0	8	8	9	9	0	0	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
2	1	1	1	8	2	3	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	6	7	*a*
	2	4	6	9	4	7	6	5	6	7	8	7	0	9	6	9	0	6	7	8	0	5	4	8	9	*b*
	3	5	7	0	8	8	9	9	0	0	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
3	1	1	1	8	2	3	2	3	4	5	1	2	3	4	6	1	2	3	5	7	1	2	3	4	5	*a*
	2	4	6	9	4	6	7	5	6	7	8	5	0	7	9	9	0	4	6	8	0	6	7	9	8	*b*
	3	5	7	0	8	8	9	9	0	0	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
4	1	1	1	8	2	3	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	7	*a*
	2	4	6	9	4	6	7	5	6	7	8	0	7	9	6	9	6	0	7	8	0	5	4	9	8	*b*
	3	5	7	0	8	8	9	9	0	0	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
5	1	1	1	8	2	3	2	4	3	5	1	2	3	5	7	1	2	3	4	6	1	2	3	4	5	*a*
	2	4	6	9	4	7	5	6	6	7	8	0	4	6	9	9	7	5	0	8	0	6	9	7	8	*b*
	3	5	7	0	8	8	9	9	0	0	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
6	1	1	1	8	2	3	2	4	3	5	1	2	3	4	5	1	2	3	4	6	1	2	3	5	7	*a*
	2	4	6	9	4	7	5	6	6	7	8	7	9	0	6	9	0	5	7	8	0	6	4	8	9	*b*
	3	5	7	0	8	8	9	9	0	0	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
7	1	1	1	8	2	3	2	4	3	5	1	2	3	4	5	1	2	3	4	6	1	2	3	5	7	*a*
	2	4	6	9	4	7	5	6	6	7	8	0	9	7	6	9	7	5	0	8	0	6	4	8	9	*b*
	3	5	7	0	8	8	9	9	0	0	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
8	1	1	1	8	2	3	2	5	3	4	1	2	3	4	5	1	2	3	6	7	1	2	3	4	5	*a*
	2	4	6	9	4	7	6	7	5	6	8	0	9	7	6	9	5	4	8	0	0	7	6	9	8	*b*
	3	5	7	0	8	8	9	9	0	0	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
9	1	1	1	2	4	6	5	3	7	2	1	2	3	4	5	1	2	3	4	5	1	2	3	6	7	*a*
	2	4	6	8	8	9	7	5	3	4	8	7	6	9	0	9	0	8	7	6	0	5	4	8	9	*b*
	3	5	7	9	0	0	8	9	0	6	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
10	1	1	1	3	5	7	2	6	4	2	1	2	3	4	6	1	2	3	4	6	1	2	3	4	5	*a*
	2	4	6	8	8	9	7	5	3	4	8	5	7	9	0	9	0	5	7	8	0	9	6	8	7	*b*
	3	5	7	9	0	0	8	9	0	6	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
11	1	1	1	3	5	7	2	6	4	2	1	2	3	4	6	1	2	3	4	5	1	2	3	4	6	*a*
	2	4	6	8	8	9	7	5	3	4	8	5	7	9	0	9	0	6	8	7	0	9	5	7	8	*b*
	3	5	7	9	0	0	8	9	0	6	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
12	1	1	1	3	5	7	2	6	4	2	1	2	3	4	5	1	2	3	4	6	1	2	3	4	6	*a*
	2	4	6	8	8	9	7	5	3	4	8	0	6	9	7	9	5	7	8	0	0	9	5	7	8	*b*
	3	5	7	9	0	0	8	9	0	6	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
13	1	1	1	3	5	7	2	6	4	2	1	2	3	4	6	1	2	3	4	5	2	3	4	1	6	*a*
	2	4	6	8	8	9	7	5	3	4	8	9	5	7	0	9	0	6	8	7	5	7	9	0	8	*b*
	3	5	7	9	0	0	8	9	0	6	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
14	1	1	1	2	4	6	5	3	2	3	1	2	3	5	7	1	2	3	4	5	1	2	3	4	6	*a*
	2	4	6	8	8	9	7	5	7	4	8	4	0	6	9	9	6	8	7	0	0	5	7	9	8	*b*
	3	5	7	9	0	0	8	9	0	6	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
15	1	1	1	2	4	6	5	3	2	3	1	2	3	4	5	1	2	3	4	6	1	2	3	5	7	*a*
	2	4	6	8	8	9	7	5	7	4	8	6	7	9	0	9	5	0	7	8	0	4	8	6	9	*b*
	3	5	7	9	0	0	8	9	0	6	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
16	1	1	1	3	2	7	5	6	4	2	1	3	4	6	2	1	2	3	4	5	1	2	3	4	6	*a*
	2	4	6	8	8	9	7	5	3	4	8	7	9	0	5	9	7	6	8	0	0	9	5	7	8	*b*
	3	5	7	9	0	0	8	9	0	6	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
17	1	1	1	3	2	7	5	6	4	2	1	2	3	4	5	1	2	3	4	6	1	2	3	4	6	*a*
	2	4	6	8	8	9	7	5	3	4	8	7	6	9	0	9	5	7	8	0	0	9	5	7	8	*b*
	3	5	7	9	0	0	8	9	0	6	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
18	1	1	1	3	2	7	5	6	4	2	1	2	3	4	6	1	2	3	4	5	1	2	5	4	6	*a*
	2	4	6	8	8	9	7	5	3	4	8	9	5	7	0	9	7	6	8	0	0	5	7	9	8	*b*
	3	5	7	9	0	0	8	9	0	6	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
19	1	1	1	3	2	7	5	6	4	2	1	2	3	4	5	1	2	3	4	6	1	2	3	4	6	*a*
	2	4	6	8	8	9	7	5	3	4	8	9	6	7	0	9	5	7	8	0	0	7	5	9	8	*b*
	3	5	7	9	0	0	8	9	0	6	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*
20	1	1	1	3	2	7	5	6	4	2	1	2	3	4	5	1	2	3	4	6	1	2	3	4	6	*a*
	2	4	6	8	8	9	7	5	3	4	8	9	6	7	0	9	7	5	8	0	0	5	7	9	8	*b*
	3	5	7	9	0	0	8	9	0	6	*a*	*a*	*a*	*a*	*a*	*b*	*b*	*b*	*b*	*b*	*c*	*c*	*c*	*c*	*c*	*c*

according to their rest figures. If we use the list of SCHROETER, then the rest figures of the triplets of the system of NETTO are resp.:

N $(01..a..)_{cyc.}$ all VII, $(0..6.8..)_{cyc.}$ ¹) all VIII.

Their possible decompositions into principal five-sides are:

I	none		
II	two,	see **1** and **2**	in the preceding table
III	two,	„ **3** „ **4**	„ „ „
IV	none		
V	three,	„ **5, 6, 7**	„ „ „
VI	one,	„ **8**	„ „ „
VII	one,	„ **9**	„ „ „
VIII	four,	„ **10, 11, 12, 13**	„ „ „
IX	two,	„ **14** and **15**	„ „ „
X	five,	„ **16, 17, 8, 19, 20**	„ „ „

According to 4 these decompositions now give rise to 20 triple systems, among which occur with certainty all possible systems; however, they can be identical mutually and to **K** or to **N**. We now remark that VI and VII can be completed in but one way; so as soon as these rests occur the system is identical to **8**, resp. **9**; from this follows already that **K** and **8**, and likewise **N** and **9** are of the same type (see table page 292).

Now rest figure VII appears for **11** according to the triplet 37*a*; VI on the contrary for:

1, 2, 3, 4, 5, 6, 7, 10, 12, 13, 14, 15, 16, 17, 18, 19, 20

resp. according to the triplets:

123, 123, 145, 167, 123, 123, 47*a*, 37*a*, 35*c*, 57*b*, 56*a*, 79*c*, 49*a*, 27*a*, 18*a*, 35*c* and 60*b*;

so **11** is identical to **9** and **K**, the remaining are identical to **8** and **N** and we have proved:

that except the two known forms no triple systems of thirteen elements exist.

At the same time is evident that to recognise a given system it is sufficient to find a few rest figures until one meets either VII (or VIII in greater number than six) or II, III, V, VI, IX or X.

The preceding has moreover given a method ²) to determine the

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¹) The cyclic order is here: 0 1 2 3 4 5 6 7 8 9 *a b c*.

²) Compare DE VRIES *Versl. en Meded. Kon. Akad. v. Wet.* VI, p. 13, where in a more restricted sense the same method is used to trace the (exclusively *regular*) principal poly-sides of the Cff. $-_n$. Such a principal poly-side however determines a triple system and reversely. Indeed, the cyclic systems of 13 and 15 appear already in the work of DE VRIES (l. c. p. 16 and 17), however without being regarded as such.

number of triple systems for arbitrary n (if only $\equiv 1$ or 3, mod. 6), i.e. to classify all diagonalless

$$Cff. \left\{ n_{\frac{n-1}{2}} \; , \; \left(\frac{n(n-1)}{2\,.\,3}\right)_3 \right\},$$

namely:

1. by starting from all possible:

$$Cff. \left\{ (n-3)_{\frac{n-7}{2}} \; , \; \left(\frac{(n-3)\,(n-7)}{6}\right)_3 \right\},$$

2. by enumerating the Cff. of its diagonals, those are:

$$Cff. \left\{ (n-3)_3 \; , \; \left(\frac{3(n-3)}{2}\right)_2 \right\},$$

3. by investigating in how many ways each of these Cff. can break up according to its lines into three principal $\frac{n-3}{2}$ sides,

4. by every time assuming the lines of such a poly-side to be convergent to one point and these three points to be collinear,

5. by arranging the obtained systems in types.

Already for $n = 15$, however, this method is checked by the absence of the classification of Cff. $(12_4\,, 16_3)$ necessary for 1, of which only some six forms have been enumerated[1]). Let us restrict ourselves to the best known and most regular form, of HESSE:

A	1	2	3	4
5	a	b	c	d
6	b	c	d	a
7	c	d	a	b
8	d	a	b	c

in which each point of the quadruplet $abcd$ is collinear to the points of the two other quadruplets in the same row of column, then *three* types of triple systems of 15 elements appear:

I. Complement $\quad x\,a\,b,\; x\,c\,d,\; x\,12,\; x\,34,\; x\,56,\; x\,78,$
$y\,a\,c,\; y\,b\,d,\; y\,13,\; y\,24,\; y\,57,\; y\,68,$
$z\,a\,d,\; z\,b\,c,\; z\,14,\; z\,23,\; z\,58,\; z\,67,$
$x\,y\,z.$

All rests are A, the system is identical to the cyclic one[2]):

(1 . 2 . . 5 . . .) ; (1 . 3 . . . 9 . . .) ; (1 . . . 6 . . . 11 . . .).

II. Complement $\quad x\,a\,b,\; x\,c\,d,\; x\,12,\; x\,34,\; x\,56,\; x\,78,$
$y\,a\,c,\; y\,b\,d,\; y\,13,\; y\,24,\; y\,58,\; y\,67,$
$z\,a\,d,\; z\,b\,c,\; z\,14,\; z\,23,\; z\,57,\; z\,68,$
$x\,y\,z.$

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[1]) Comp. the author's dissertation; "Bijdragen tot de theorie der configuraties", Amsterdam 1907, § 86.

[2]) L. HEFFTER, *Math. Annalen*, Vol. 49.

There are three rests A, namely of

$$x\,y\,z, \quad x\,56 \quad \text{and} \quad x\,78;$$

there are four rests B, i. e. of the type of the Cf. $(16_3, 12_4)$ of DE VRIES of the composition

B	1	2	3	4
5	a	b	c	d
6	b	c	d	a
7	c	d	a	b
8	d	a	b	c

These rests appear for $x\,a\,b$, $x\,c\,d$, $x\,12$, $x\,34$.

The other rests are of other types.

III. Complement $x\,a\,b$, $x\,c\,d$, $x\,12$, $x\,34$, $x\,58$, $x\,67$,
$y\,a\,c$, $y\,b\,d$, $y\,13$, $y\,24$, $y\,56$, $y\,78$,
$z\,a\,d$, $z\,b\,c$, $z\,14$, $z\,23$, $z\,57$, $z\,68$,
$x\,y\,z$.

Only $x\,y\,z$ has rest A, there are no rests B, all other rests are of other types.

Whether by completing other Cff. $(16_3, 12_4)$ other systems than the three above-mentioned will appear, remains undecided; at any rate B will lead in at least *one* way to II as it appears among its rests.

Anatomy. — "*About the function of the ventral group of nuclei in the thalamus opticus of man.*" By Prof. C. WINKLER and Dr. D. M. VAN LONDEN.

The following remarkable case was offered to our observation in the neurological clinical department of the Binnengasthuis.

An unmarried woman, aged seventy-seven, not having suffered previously of any serious illness, and somewhat dull of hearing during the last years, got one single but severe fit of dizziness three weeks before her admittance.

On Jan. 8th 1908 she was found in her room unconscious, and transported thence to the Binnengasthuis, on arrival there she was slightly wandering in her mind. This state continued for three days, afterwards she made no complaints either of pain or of paraesthesia. Incontinence never occurred. There was found sclerosis of the arteries and dilatation of the heart. The urine contained $^1/_4$ $^0/_{00}$ of albumen and hyaline-cylindres. After three months death ensued caused by pneumonia. Clinical examination of the different organs of sense in this woman gave the following results:

Smell and *taste* are normal.

Sight has diminished on account of a beginning senile cataract, and has on both sides been reduced to $^{6}/_{24}$. The fundus oculi is plainly visible and does not show any alterations. There is no restriction of the visual area worth mentioning.

Hearing is very bad during the first time after her admittance. She is almost completely deaf. The whispering voice is not heard on either sides. After three weeks this disturbance is restored so far, that on the left the whispering voice is distinguished to a distance of 3 M. This degree of dullness of hearing continued till her death.

On both sides the tympanic membrane has suffered slight selerotical degenerations.

The *sensibility* of the body is in all respects normal to the left, *on the contrary to the right it has considerably decreased*, in the following manner:

the tactile sensibility is entirely lost in the right hand and foot, in the lower part of arm and leg it has suffered great disturbance, somewhat less in shoulder and hip, and still less in the right half of the trunk, whilst in the right half of the face hardly any disturbance is to be observed. *The difference between the head and the point of a pin* is badly distinguished on the right side, except in the face. The latter disturbance, like that of the tactile sensibility, has its boundaries towards the left in the mid-dorsal and mid-ventral lines of the trunk and is most marked in hand and foot.

The *pain-sensibility* of the skin has likewise diminished to the right. Piercing of the skin is not at all perceived in the extremities, only feebly in the trunk, but almost normally in the face.

On the contrary *pinching* or *squeezing* of the deeper situated portions produces a much sharper perception of pain to the right than to the left. Vehement repelling movements are occasioned by it.

The perceptions of *intense cold* and *intense heat* have suffered great decrease in the right extremities, to a less degree in the right half of the trunk, whilst the disturbance is feeblest in the face.

Passive movements communicated to the fingers, the hand, the toes or the foot of the right side, are not perceived at all, however swift and extensive these movements may be. Movements performed with the articulations of the right elbow or knee are perceived badly, for movements with the articulations of the right hip and shoulder the perception is nearly normal. The patient has lost all notion as to the manner in which her right hand and foot are *placed in space*, as regards the position of knee and elbow her perception is likewise inaccurate but to a less degree.. The position of the upper-arm and leg is ascertained with tolerable accuracy. There is complete *astereognosis* of the right hand. Not a single object put into this hand is recognized. The patient does not know whether she has got something in this hand or not. Oftenest she drops it.

All these disturbances of sensibility to the right remained stationary during the three months the woman was under observation.

On the contrary the motility of the right limbs had suffered only slightly. In the week after the lesion she complained of a certain feebleness of the right extremities.

A paralysis however has never been observed. The complaint was a passing one, and the only fact ascertained was that the right shoulder hung somewhat lower than the left one. Rapid as well as subile movements could be performed with the right extremities, e. g. to count money, or to bring the finger to the top of the nose, were done nearly as well by the right hand as by the left. *Here is only a slight right-sided cerebral ataxy, and there does not exist any vestige of athetosis, or choreic or other involuntary movements.* The dynamometer in the hand reached 50 K. on both sides.

The skin reflex-actions, as the abdominal, cremaster- and plantar-reflex-actions, are normal and on both sides equal. The deep reflex-actions, those of the tendo Achillis and of the knee are not increased, there is no clonus of foot or knee. Neither is there a distinct difference of tonus, nor any atrophy in the muscles of the two halves of the body. There have been no disturbances of speech or articulation. As the patient had never learned reading or writing, possible disturbances in reading or writing were not to be stated. Her condition remained unaltered until her death on the 24th of March 1908.

The brains, which were kindly put at our disposition from the laboratory of Prof. KUHN, were indurated in formaline for a few days. Thereupon frontal sections of 1 cm. were made through both hemispheres. The *only* degeneration that may be observed macroscopically is a focal destruction in the medial and caudal portions of the left thalamus opticus.

Consequently for the purpose of microscopical examination there was made a series of frontal sections through the left hemisphere, the most proximal sections of these passing through the caudal ends of the frontal convolutions, the temporal pole and the commissura anterior, whilst the most caudal section passes behind the caudal end of the fissura Sylvii, through the caudal border of the gyrus supramarginalis, the praecuneus and the splenium corporis callosi.

The nucleus caudatus, the nucleus lenticularis, the capsula interna and the frontal end of the thalamus opticus have not suffered any alteration. Neither has the whole of the nucleus anterior. About halfway the sections through the thalamus, the frontal commencement of the focal softening is found, as a small irregular square in the nucleus lateralis (fig. 1). The hearth consist of leucocytes, lying close to one another, in its wall the capillary vessels are found distended and surcharged with blood-cells.

In the following sections the hearth is rapidly expanding (see fig. II). Irregularly shaped, it is situated within the ventral nuclei [1]), destroys the largest part of the nucleus ventralis *b*, encompasses like this nucleus the "centre médian" of Luys, and enters into the ventral nucleus *a* until near the regio subthalamica. The "Gitterschicht", the lamina medullaris externa and the regio subthalamica are untouched by it; consequently both, the lateral medullary mass of the red nucleus and the strata of the lemmiscus, remain free from damage.

In the same region is found a smaller focus, as yet apparently separate, (but in reality connected with the larger hearth) in the principal portion of the nucleus medialis.

A little more caudalward (see fig. III) the hearth attains its largest extension. It is now situated in the ventral nuclei *a*, *b* and *c*, that are almost completely destroyed, it sends a narrow branch into the nucleus medialis, and proceeds straitened wedge-like towards the regio sub-thalamica, where it approaches very closely the radiations of the lemniscus-fibres and intercepts these.

Still more caudalward (see fig. IV) the position of the hearth has become such, that the ventral nucleus *a* is left free, whilst the nuclei *b* and *c* and likewise the posterior nucleus are absorbed by it. The corpus geniculatum mediale forms here likewise part of the hearth (but the radiation from the bracchium conjunctivum corporis quadrigemini postici into the nucleus gen. medialis is left uninjured). The hearth continues by a long and narrow branch along the ventral side in the pulvinar thalami optici (see fig. V), ending there.

The corpus geniculatum laterale is no where touched by the hearth. Neither is the so-called "Gitterschicht" of Arnold.

From this focus secondary degenerations start into different areas, these degenerations are distinguished partly by the presence of granular cells, partly by the absence of medullated fibres in lighter-coloured areas in preparations after the Weigert-Pal method.

In the thalamus, the frontal end of which does not show any degenerative alterations (see fig. I) the posterior part of the medial principal nucleus has assuredly lost fibres, especially in the portion situated caudal of the hearth. Such is likewise the case with the "Gitterschicht", although it is no where touched directly by the hearth. In the neighbourhood of this latter a great number of the fibres passing the Gitterschicht in their course from the thalamus towards the retro-lenticular portion of the capsula interna, are degenerated. Those degenerated fibres gather into an area, lying close to the "Gitterschicht", an area, which in preparations made after WEIGERT-PAL's method, contrasts with its surroundings by its being light coloured, against the black coloured retro-lenticular portion of capsula. (see fig. IV*a*) 2).

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[1]) von Monakow's nomenclature of the nuclei Thalami is followed.

Situated at first lateral of the "Gitterschicht" (see fig. IV*a*), this area may be pursued caudalward (fig. IV*a*, fig. Va_1a_2, fig. VI$a_1a_2a_3$) and frontalward (fig. IIIa_1a_2 and fig. IIa_2). In the caudal sections its ventral boundary is the medullary triangle surrounding the corpus geniculatum externum (W' in fig. III), expanding thence both in the stratum sagittale externum and in the stratum sagittale internum (see fig. III and fig. IV). In frontal sections this field is situated in the capsula interna, medialward from the caudal ending of the putamen nuclei lenticularis (fig. IIa_2).

This degenerated area may be followed in three directions:

1st in the medullary rays of three temporal convolutions (see fig. I—VIIa_1) least in the gyrus temporalis I,

2nd in the splenium corposis callosi (see fig. VI and VIIa_3)

3rd in the medullary rays of the gyrus supramarginalis and still for a large part in the gyrus centralis posterior (see fig. I—VIIa_2). When examined in glycerine preparations the medulla of these gyri is thickly interspersed with granular cells.

Summing up the abovetold facts, we find some definite disturbances of perception in an old woman, after a lesion produced by a hearth of degeneration strictly localized within the left thalamus. These disturbances are:

1st Temporary deafness on both sides, leaving as its stationary result a certain degree of dullness of hearing on both sides.

2nd On the right side a chronic loss of sensibility in all qualities of sense of the skin and the deeper-situated parts, almost complete in the distal ends of the extremities, less marked in the trunk and in the roots of the extremities, unimportant in the face. All this is not accompanied by any choreic movements on that side, whilst there is found only a very slight ataxy to the right.

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2) In the drawings the areas are represented too light-coloured.

Without any doubt these disturbances are dependent on that hearth.

The loss of hearing is probably connected with the destruction of the corpus geniculatum mediale. This destruction, together with the secondary atrophy towards the temporal radiation (see a_1 in the figures), suffice to explain a certain loss of hearing, according to experiments made by different investigators after very different methods.

It is only to be noted as a remarkable fact that the patient was at first completely deaf on both sides, although the lesion was only at the left side. Remarkable too is the rapid way in which an important amelioration of this deafness set in.

The area of degeneration (a_1 in the figures) does not attain in the first place the medullary cone of the temporal convolution turned towards the fissura Sylvii, but is situated in preference in the two other temporal convolutions. This may be a reason, that she did hear and understood the spoken word.

It is formed by degenerated fibres, arriving thither both from the stratum sagittale externum and from the stratum sagittale internum, as becomes evident especially in the more frontal sections. In the sections made more caudalwand, a degenerated fascicle going towards the splenium corporis callosi may also be pursued.

Perhaps these facts may add something to an eventual explanation of the incomplete deafness on both sides after focal disturbances on one side of the brain. But leaving this aside as less important, we desire only to call attention to the chief point of this interesting case.

The *ventral groups of nuclei* in the thalamus opticus, more especially their caudal portions — and these nuclei only, with the exclusion of all others — *are found softened in the cerebrum of a person, who during life had lost all sensibility in the distal ends of the crossed extremities without choreic movements, without intensive cortical ataxy on that side,* whilst the sensibility remained nearly intact in the face, and had suffered some decrease at the proximal ends of extremities.

Similar strictly defined hearths of degeneration are very rarely found in hemi-anaesthesia, but they contribute important data to the study of the intra-cerebral course of the tracts for the general sensibility.

These tracts are less known by far than the intracerebral course of the tracts for sight and hearing.

Since Türck in 1850 by his experimental researches gave the first impulse to the study of the intra-cerebral sensibility tracts, there has appeared an enormous amount of literature on this subject, which has been recapitulated with sufficient accuracy in the dissertation of Long[1] (under guidance of Déjerine). The chief result of this mass of labour was, that at present it has become nearly generally assumed that the thalamus opticus, amongst other functions, also contributes to provide for the sensibility of the crossed half of the body.

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[1] Edouard Long. Les voies centrales de la sensibilité générale. (Étude Anatomo-clinique). Thèse de Paris. 1899.

From the side of the school of DÉJÉRINE this opinion has been put forth with marked emphasis in the excellent book of ROUSSY [1]), who includes the disturbance of sensibility in the crossed half of the body in his "syndrome thalamique."

But not even in this work is treated a hearth localized so exclusively on the thalamus opticus [2]). The strict localization noted in our case justifies the thesis:

The caudal portions of the ventral groups of nuclei in the thalamus opticus take a similar part in the central projection of the sensibility of the skin and of the deeper portions in the distal ends of the crossed extremities (less completely of the trunk and of the roots of the extremities, hardly at all of the face) as that taken by the corpus geniculatum mediale in the central projection of the impressions from the cochlea and by the corpus geniculatum laterale in the projection of the impressions from the retina.

A case, closely resembling the one given here, has been described by VON MONAKOW [3]). Unfortunately he could not dispose of sufficient clinical data, especially as regards the question whether there had been hemianaesthesia during life. On the other hand he has described with the most careful accuracy the secondary atrophic degenerations, consequent to the loss of the posterior ventral nuclei, these degenerations being nearly the same as in the case related in the foregoing. It appears to us that in this latter case the gyrus centralis posterior receives a greater number of fibres from the atrophic area than in this well-known case of VON MONAKOW, offering nevertheless many striking points of resemblance with it.

It is moreover an important fact that the face remained almost wholly exempt from the loss of sensibility. Perhaps this is somehow connected with the fact that the median principal nucleus and the centre médian remained likewise almost wholly free from the degenerative hearth. For in animals the secondary tracts of the trigeminus have been traced principally to the centre médian (WALLENBERG [4]) together with the ventral nucleus, others also believe the medial nucleus to be connected with the N. trigeminus (ARRIËNS KAPPERS[1]); besides animals with a powerfully developed trigeminus (e. g. the mole) possess a large medial nucleus. Consequently in regard to this case the possibility is not to be denied that the medial nucleus may stand in some closer relation to the sensibility of the face than the ventral does.

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[1]) GUSTAVE ROUSSY. La couche optique et le syndrome thalamique. Paris, Steinheil. 1907.

[2]) ROUSSY l. c. Compare cas JOSSAUME p. 229.

[3]) C. VON MONAKOW. Zur Anatomie und Physiologie des unteren Scheitelläppchens. Arch. f. Psych. 1899. XXXI S. 1—74. Fall D'auj. Also conf. L. EDINGER, Erkrankung des Thalamus opticus. Bd. XXI. Arch. f. Ps. 1899. S. 657.

[4]) ADOLF WALLENBERG. Secundaire Bahnen aus dem frontalen sensiblen Trigeminuskerne des Kaninchens. Anat. Anz. XXVI. 1905. S. 145—155.

The above described case represents an almost unique experiment taken by Nature, and it demonstrates, *that isolated destruction of the ventral thalamus-nuclei may be accompanied by loss of all sensible perception in the distal ends of the crossed extremities.*

EXPLANATION OF THE FIGURES.

Fig. I—VII, frontal sections through the left hemisphere. Fig. I is a section frontal from the red nucleus, which hits the corp. subthalamicum; the frontal beginning of the hearth. Fig. II through the red nucleus, the retrolenticular portion of the capsula interna here begins. Fig. III through the largest expansion of the hearth, the c. quadr. anterius is sectioned. Fig. IV through the corpora geniculata and pulvinar thalami. Fig. V the caudal end of the hearth in the pulvinar thalami.

In all sections *a.* indicates the area of degeneration in the retro-lenticular portion of the capsula interna, situated lateral from the Gitterschicht, a_1 a_1 the radiation of the degenerative field towards the temporal radiation, $a_2 a_2$ the radiation towards the gyrus supramarginalis and towards the gyrus centralis posterior, a_3 a_3 the radiation towards the corpus callosum.

Fig VI, the section through the splenium corp. callosi. The degenerative areas.

Fig. VII, through the splenium corp. callosi and the tapetum.

In all figures the signification of the letters employed is as follows:

cap. n. c. = caput nuclei caudati, caud. n. c. = cauda nuclei caudati, c. c. = corpus callosum, c. f. = columna fornicis, f. f. = fimbria fornicis, f. c. = fissura centralis, f. i. p. = fissura interparietalis, f. p. c, = fissura postcentralis; f. S. = fissura Sylvii, r. a. f. S. = ramus ascendens fissurae Sylvii, G. C. a. = gyrus centralis anterior, G. C. p. = Gyrus centralis posterior, G. s. M. = Gyrus supramarginalis, G. L. = gyrus lingualis, G. F. = gyrus fornicatus, G. H. = gyrus hippocampi, G. P_1 = gyrus parietalis superior, G. Para C. = gyrus paracentralis, G. Pr = gyrus praecunei, G. O. T. = gyrus occipito-temporalis, GT_1, GT_2, GT_3 = gyri temporales, l. m. e. = lamina medullaris externa thalami, l. m. i. = lamina medullaris interna, p. p. = pes pedunculi, pulv. = pulvinar thalami, n. ant. = nucleus anterior thalami, n med. = nucleus medialis thalami, n. lat. = nucleus lateralis thalami, n. ventr. (a. b. c.) = nucleus ventralis thalami (a b. c.), Gitt. = Gitterschicht, n. c. = nucleus caudatus, n. l. = nucleus lenticularis, N. R. = nucleus ruber, m. d. N. R. = medulla dorsalis nuclei rubri, s. n. = substantia nigra, c. L. = corpus subthalamicum, c. m. L. = centre médian Luys), spl. c. c. = splenium corporis callosi, s.s. ext. = stratum sagittale externum, s. s. int = stratum sagittale internum (radiation of GRATIOLET), str. t = stria terminalis, tap. = tapetum, W. = stratum medullare corporis geniculati lateralis (WERNICKE's triangular area), c. g. l. = corpus geniculatum laterale, c. g. i. = corpus geniculatum mediale.

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[1] C. A. ARRIËNS KAPPERS. Weitere Mitteilungen über die Phylogenese des Corp. striatum und des Thalamus. Anat. Anz. 1908. Bd. XXXIII. No. 13 und 14, S. 321.

Physics. — *"On the kinetic derivation of the second Law of Thermodynamics."* By Dr. O. Postma. (Communicated by Prof. H. A. Lorentz.)

§ 1. In a previous paper[1]) I tried to set forth how an ensemble of molecular systems possessing only kinetic energy may be thought gradually to pass to a state in which all the combinations of place and also all the combinations of velocity of the molecules occur with the same frequency. In this final condition the molecules of by far the majority of the systems of the ensemble will, as was shown, be distributed about uniformly over the vessel and have Maxwell's distribution of velocities.

This result, however, requires some amplification.

As the problem of the distribution of place and that of the distribution of velocity were treated quite separately, the above-mentioned result implies only, that in the end the molecules will be distributed uniformly over the vessel *for all the velocities together*, and that they will have Maxwell's distribution of velocities *for the vessel considered as a whole*. This, however, is not what is generally understood by uniform distribution over the vessel and Maxwell's distribution of velocities; we mean by this that even for a limited amount of velocities the molecules will be spread about uniformly over the vessel, and that even for a limited portion of the vessel Maxwell's distribution of velocities will hold on the main. So the question remains, how this result may be obtained.

Let us first observe that in a canonical or microcanonical ensemble the uniform distribution of place and Maxwell's distribution of velocities in the latter sense is really obtained. This is very easily seen for the canonical ensemble. It is, however, also the case for a microcanonical ensemble, where the frequency of a certain distribution of place and velocity is proportional to the number of combinations possible. This number of combinations may be given in the form $Ce^{-\iint f \log f \, do d\omega}$ just as it is given in the form $Ce^{-\int f \log f \, d\omega}$ when only the distribution of the velocities is considered. So in the most frequently occurring system $-\iint f \log f \, do d\omega$ or $-H$ is maximum. With given kinetic energy this is the case, if

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[1]) These Proc. X, p. 390.

$f = ae^{-b(\xi^2+\eta^2+\zeta^2)}$, where a and b are real constants, so that for this system MAXWELL's distribution of velocities holds for any small part of the vessel, and also the density is constant throughout the vessel for one definite velocity. That for the great majority of the systems the distribution of place and velocity differs little from the maximum occurring one may be shown in the same way as it is shown when the distribution of place and velocity is considered separately.

It is, however, easy to see that if an ensemble arises, not a microcanonical one, indeed, but one, for which the mean density becomes constant for finite but small extension elements, by approximation the same result will be obtained as we have for a microcanonical ensemble, viz. uniform distribution throughout the vessel and MAXWELL's distribution of velocities, and that with greater accuracy as the elements are smaller. So we shall have a kinetic derivation of the 2nd law of thermodynamics, if we can show that an arbitrary ensemble of systems with a definite kinetic energy passes into such a "rough" microcanonical ensemble. So this has again led us to the quantity called "entropie grossière" by POINCARÉ, for if Π, the mean density over the elements σ, becomes constant, $\Sigma\, \Pi \log \Pi\ \sigma$ or the entropie grossière decreases. It seems to me that we might demonstrate in the following way that Π becomes constant in course of time.

Let us in the first place once more consider the ensemble of planets or one-dimensional moving molecules discussed in § 2 and § 3 of the above-mentioned paper. It was shown that this ensemble moves in such a way that finally all places occur equally frequently. This was the case for all the velocities together and happened just because all kinds of velocities occurred for the systems. If, however, the total amount, over which the velocities of the systems (planets or molecules) extend, is divided into small, but finite portions, it will also hold for these amounts separately, if we only take the time long enough. So when these amounts extend from ω_1 to $\omega_1 + \Delta\omega_1$, from $\omega_1 + \Delta\omega$ to $\omega_1 + 2\Delta\omega$ etc. the systems with velocities lying between ω_1 and $\omega_1 + \Delta\omega$ will finally be uniformly distributed over all the values l lying between 0 and 2π; in the same way the systems with velocities between $\omega_1 + \Delta\omega$ and $\omega_1 + 2\Delta\omega$ etc. Each of the horizontal strips of fig. 1 lying above each other contains then the same number of representing points.

If instead of an ensemble of single planets or single molecules we take an ensemble of systems of n molecules each but disregard the collisions, the same reasoning will hold. The whole of the representing points now moves, however, in a $6n$-dimensional space, and instead of the axis of distances and the axis of velocities we get now the space of coordinates and the space of velocities. Also if we do not neglect the collisions a motion of the ensemble will take place in the moments between the collisions in the indicated direction, so to the state with uniform mean density in the narrow strips extending lengthwise over a small but finite distance, bounded by the same combinations of velocities (symbolically represented by the horizontal regions a of fig. 2). In consequence of the collisions, however, the mean density in narrow vertical regions approaches uniformity. Nor need these

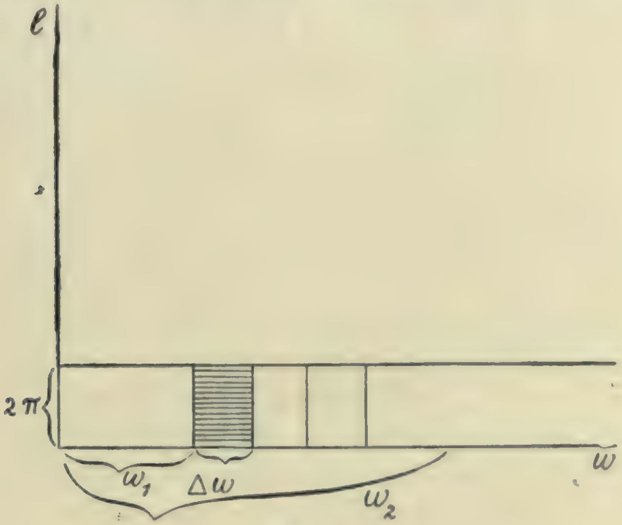

Fig. 1.

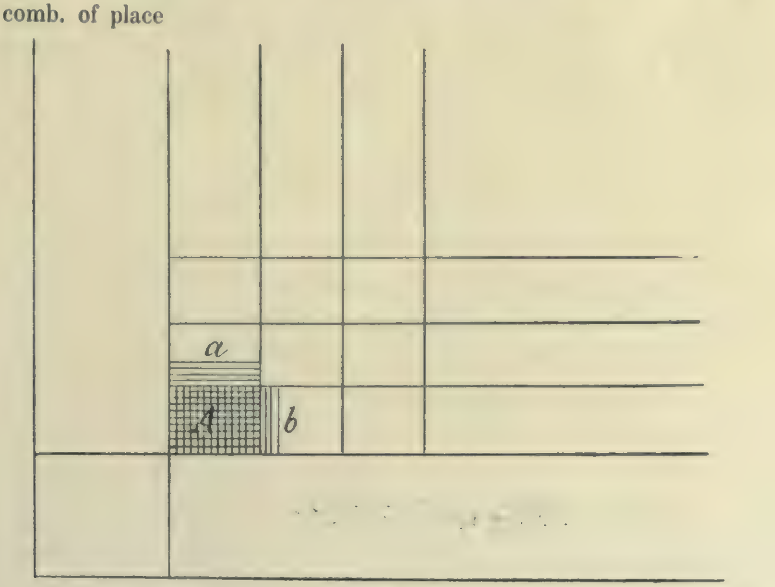

Fig. 2.

regions extend over the total amount of possible combinations of place, but the approach to uniformity is also found over finite small portions of this amount, (the regions b). What happens now if the two actions take place simultaneously? In the collision the representing points shift in horizontal direction, which modifies the distribution in the regions a, and the first action, which would make the distribution over the regions a uniform, is counteracted. This continues to be the case, as we think the regions a infinitely narrow; if however, we consider an element from the figure, the horizontal dimension of which is indicated by a, and the vertical dimension by b (the rectangle A), then the distribution in the elements A lying one above the other will also approach to uniformity by the first action whereas the disturbing influence with which the second action counteracts the first, will continually decrease and approach to zero. So it seems to me that we may assume that the mean density in the elements A lying above each other becomes the same in course of time; this reasoning will, however, also hold for the elements lying side by side in horizontal direction (if we take now the second action as the principal one, and the first as the disturbing action), so that we get a "rough" microcanonical ensemble in the end 1).

If the above reasoning is correct, we have obtained the result that every arbitrary ensemble of molecule systems with purely kinetic energy proceeds towards a state where uniform distribution of place and MAXWELL's distribution of velocities is most frequent. In the meantime we must assume that every system in itself has a reversible motion and so after some time it will get again very near to its initial state, and will do so repeatedly. Whether BOLTZMANN's $H = \iint f \log f \, do \, d\omega$ will decrease for the majority of the cases depends on the initial state of the ensemble. It is conceivable that this state is such that the majority of the systems are nearer to the state occurring finally maximum than is the case for a micro-canonical ensemble; then the H would increase instead of decrease for those systems. It is, however, evident, that this will not be the case for an ensemble that represents a system in which recently some disturbance of equilibrium has taken place. For such a system H will most probably decrease.

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1) It would be doing GIBBS an injustice if we did not admit, that in his Statistical Mechanics he already pointed to this remaining constant of the entropie fine, in opposition to the decrease of the entropie grossiere when he says treating the analogy of the coloured liquid: "If treating the elements of volume as constant ... etc." p. 145.

§ 2. Now the question may be raised what place we have to assign to BOLTZMANN's proof that $H = \iint f \log f \, do \, d\omega$ would decrease for an "ungeordnetes" system with regard to the above reasoning and the one preceding it. H seems to have to decrease for such a system, which as ZERMELO and others pointed out can hardly be always the case for one definite system, and can only be assumed as occurring in general for an ensemble.

In the first place we must observe with regard to this that by no means certainty prevails that a system which is in an "ungeordnet" state at a certain moment, will continue to be in such a state.

In the second place the properties of such a system, as BOLTZMANN applies them in the derivation of the variation of the function H in consequence of the collisions (see form. 17 and 105), can occur for one definite system with a sufficient degree of accuracy only when the elements $d\omega$, $d\lambda$ etc. occurring in these formulae, are taken rather large. There are, however, also objections to this (as that it is assumed that in a collision of two molecules the velocity-points always get outside the elements $d\omega$ and $d\omega_1$).

Independent of the size of the elements the property of being "ungeordnet" cannot occur for one definite system, it can, however, for the average of a whole ensemble (or in course of time if we think the systems taken at random from a certain ensemble).

This ensemble is formed by the whole of the possible systems obtained if we think the places and velocities of the n molecules assigned to them by chance, so that every time the chance to a certain combination of place and velocity is represented by a constant function f of the coordinates and velocities. If n is large, the majority of these systems have a distribution of place and velocity the course of which is mainly indicated by the function f. It does not hold exactly for any definite system that in the neighbourhood of every molecule the number of molecules of a certain kind are determined by the size of the spacial element considered and the f holding there, but on an average it does hold for the whole ensemble. So we may say that this ensemble represents BOLTZMANN's "ungeordnetes" system. On an average $\frac{dH}{dt}$ would, therefore, be negative for this ensemble.

On further comparison of BOLTZMANN's way of treatment and the results of § 1 we meet with an important point of difference. On the whole H will decrease for the majority of the systems for an arbitrary ensemble on account of the tendency towards uniformity of density over the elements of extension indicated by A in fig. 2. This tendency proceeded from two actions, the former giving uniform density over the horizontal, the latter over the vertical regions. So we might say that the decrease of H is brought about both by the motion of the molecules (the first action) and by the collisions (the second action). The coordinates and the velocities occur also in H in the same way.

Yet Boltzmann states expressly that the H can only decrease in consequence of the collisions[1]) and he shows this as follows:

The change of H within a given surface is determined by

$$\frac{d}{dt}\sum_{\omega,0}\log f=\iint do\,d\omega\left[\frac{\partial f}{\partial t}-\log f\left(\xi\frac{\partial f}{\partial x}+\eta\frac{\partial f}{\partial y}+\zeta\frac{\partial f}{\partial z}+X\frac{\partial f}{\partial \xi}+Y\frac{\partial f}{\partial \eta}+Z\frac{\partial f}{\partial \zeta}\right)\right]$$
$$+\,C_4\,(\log f)+C_5\,(\log f).$$

If the surface is made to join the walls of the vessel, the first term is zero, the terms with X, Y, and Z are lost if we assume that there are no external forces; C_4 and C_5 denote the change caused by the collisions. The change in consequence of the motion of the molecules is equal to:

$$-\iint do d\omega\,\log.f\left(\xi\frac{\partial f}{dx}+\eta\frac{\partial f}{\partial y}+\zeta\frac{\partial f}{\partial z}\right).$$

Boltzmann shows that this integral is equal to:

$$\iint d\omega dS\,fN-\iint d\omega dS\,Nf\log f$$

which is to be integrated over the surface S, which includes the considered gas mass. From this follows that the increase in H in consequence of the motion is equal to the quantity that is brought into the surface S by the molecules. So if the gas is left to itself, this quantity will be zero, so that H does not change in consequence of the motion, but only in consequence of the collisions[2]). No doubt we shall have to look for the explanation of this difference in result to the fact that Boltzmann considers the "entropie fine", whereas above the "entropie grossière" was considered. If the elements do and $d\omega$ are taken of finite size, as must be done here, the calculations which reduce the change in H to a surface integral, must not be adopted in unmodified form.

§ 3. For a kinetic derivation of the 2nd law of thermodynamics it is necessary kinetically to define a quantity which agrees in

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[1]) See: Vol. I, p. 126, note.

[2]) Cf. Lorentz, "Abhandlungen über Theoretische Physik", Abhandl. VIII.

properties with the thermodynamic entropy. These properties are:
1. For reversible changes from one state of equilibrium into the other is $\frac{dQ}{T}$ the differential of a quantity which is defined as entropy; 2. in an isolated system which, as a whole, is not in equilibrium, but may be divided into parts which are, the total entropy increases. We saw above that in general the quantity introduced by Boltzmann

$$H = \iint f \log f \, do \, d\omega$$

decreases, also when the system does not consist of parts, each in itself in equilibrium. So if we consider a quantity proportional to $-H$ as entropy, it will certainly satisfy the second condition in by far the majority of cases. As to the first condition, this is satisfied as Lorentz has shown[2]), if $-\frac{2}{3}\mu$ is taken for the constant by which H is multiplied, in which $\mu = \frac{\text{mean kin. energy per mol.}}{\text{abs. temperature}}$. For a gas in stationary state

$$f = Ce^{-\frac{3m}{4k}\left(\xi^2+\eta^2+\zeta^2\right)} = n\sqrt{\left(\frac{3m}{4\pi k}\right)^3} e^{-\frac{3m}{4k}\left(\xi^2+\eta^2+\zeta^2\right)}$$

so that

$$-\frac{2}{3}\mu H = -\frac{2}{3}\mu N\left(\log C - \frac{3}{2}\right) =$$

$$= \frac{2}{3}\mu N \log v + \mu N \log \vartheta - \frac{2}{3}\mu N \log N - \mu N \log \frac{3m}{4\pi\mu} + \mu N$$

for which Lorentz writes:

$$\frac{2}{3}\mu N \log v + \mu N \log \vartheta + C'.$$

At a given temperature we may, accordingly, write $N\left(\log\frac{N}{v} + C\right)$ also for H, in which C still contains ϑ, no longer N and v.

Besides this entropy of Boltzmann different quantities have been kinetically defined by Gibbs, which, according to him, possess the properties of the entropy. The most prominent of them is the $-\eta$ or $-\int P \log P \, d\tau$, being the negative mean *log* of the density over the canonical ensemble which represents the system in equilibrium. As was shown by Lorentz [1]) this quantity has the property that in reversible changes of the system the differential is equal to $\frac{dQ}{T}$, in which T, the modulus of the ensemble, has the properties of the temperature. This entropy was only defined by Gibbs for the state of equilibrium. When, however, we represent a gas which is not in equilibrium by a non-canonical ensemble, and define the entropy in the same way, also the second property will hold for this entropy; the quantity $\int P \log P \, d\tau$ will namely gradually decrease if the elements $d\tau$ are not taken *infinitely* small, because each portion of the ensemble with given energy approaches to a rough micro-canonical one. In the special case considered in thermodynamics that the parts of the system are in equilibrium this will also be the case [2]).

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[2]) Cf. l.c. Abhandlung VIII.

Calculating this $-\bar{\eta}$ for a perfect gas, we find, as

$$-\bar{\eta} = \frac{\bar{\varepsilon}-\psi}{T}$$

whereas

$\bar{\varepsilon} = \frac{3}{2} NT$ and $-\frac{\psi}{T} = \frac{3}{2} N \log(2\pi mT) + N \log v$,

$$-\eta = \frac{3}{2} N + \frac{3}{2} N \log(2\pi mT) + N \log v.$$

When comparing this value with Boltzmann's entropy we must bear in mind that this T does not agree perfectly with the ϑ of Boltzmann; viz.:

$$\vartheta = \frac{\textit{mean kin. energy per mol.}}{\mu} \text{ and } T = \frac{\textit{mean kin. energy per system}}{\frac{3}{2} N}.$$

From this follows $T = \frac{2}{3} \mu \times$ mean ϑ (taken over the ensemble).

So for comparison we must take:

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[1] See Abhandlung XI.

[2] The objection advanced by Lorentz to this way of defining the entropy, that it would namely be difficult to understand how a non-canonical ensemble should be determined by a system that is not in equilibrium, does not seem to be conclusive to me. It is true, that the entropy and the ensemble are not determined in the same way as for a stationary system, but as we know more about the place and the velocities of the molecules or the way in which they have assumed their places and velocities, the ensemble is determined more accurately. If we e.g. know that everywhere a certain pressure and temperature prevails, we consider the ensemble as a sum of canonical ensembles, etc.

$$-\frac{2}{3}\,\mu\,\overline{\eta} = \mu N + \mu N \log \left(\frac{4}{3}\,\pi\mu m\vartheta\right) + \frac{2}{3}\,\mu N \log v,$$

for which we may also write:

$$\frac{2}{3}\,\mu N \log v + \mu N \log \vartheta + C'';$$

this C'', however, does not agree with LORENTZ' C'.

In this connection I will finally call attention to an objection to the use of this latter entropy introduced by GIBBS.

Purely thermodynamically the entropy is determined by the diff. equation $\frac{dQ}{T} = d\eta$. So this η contains an arbitrary additive constant. This is not the case for the kinetically defined one. BOLTZMANN's H is entirely determined by the equation $H = \iint f \log f \, do\, d\omega$ and so also the entropy $-\frac{2}{3}\,\mu H$. In the same way in GIBBS $-\overline{\eta} = -\int P \log P \, d\tau$, if the energy is purely kinetic, which we shall assume.

The same applies to the free energy ψ, thermodynamically it contains an arbitrary additive constant, kinetically it does not. This uncertainty, however, allows us to choose the constant in thermodynamics in a convenient way, which is no more possible in the kinetic theories. This constant is now chosen in such a way that the ψ for a certain gas mass (and then also the η) is equal to the sum of the ψ's of the parts (molarly not molecularly separated). This appears clearly in LORENTZ [1]). Here a gramme molecule of a certain gas is considered, and

$$\psi = -RT \log v + C \text{ derived from } \frac{\partial\psi}{\partial v} = -p = -\frac{RT}{v}.$$

Now C is chosen in such a way, that $\psi = 0$ if $v = 1$, so $C = 0$ or $\psi = -RT \log v$. Somewhat further it says: "Haben wir es nicht mit einer, sondern mit m Einheiten zu tun, die zusammen das Volum v füllen, so haben wir nebeneinander m-mal die Einheit in dem Volum $\frac{m}{v}$. Wir müssen also in $\psi = -RT \log v$ v durch $\frac{m}{v}$ ersetzen und dann mit m multiplizieren." So by definition the ψ of the whole has here evidently been put equal to the sum of the ψ's of the parts occurring side by side in the volume v.

We may also say that this has taken place by assigning another value to C for every quantity. If namely in a volume $2v$ we had two unities side by side, we should have for the first $\psi_1 = - RT \log v$, for the second $\psi_2 = - RT \log v$, so $\psi_1 + \psi_2 = - 2RT \log v$. For the total quantity we should have $\psi = - 2RT \log 2v + C$; if now we had again put $C = 0$ (so that $\psi = 0$ if $2v = 1$) then ψ would not have been $= \psi_1 + \psi_2$. The C, however, has now been chosen in such a way that $\psi = 0$ if $2v = 2$ or $C = 2RT \log 2$ and hence $\psi = - 2RT \log v = \psi_1 + \psi_2$.

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[1]) l. c. p. 236.

In connection with this we have the property that if two quantities of different gases, being in equal volumes at the same T, are mixed in the same volume at the same T, the free energy remains the same, whereas it decreases if this is done with two quantities of the same gas. A similar property exists for the entropy (GIBBS's paradox). How is this now for the kinetically defined entropy or free energy? To answer this question we shall successively discuss: 1 is the entropy of an homogeneous gas mass in a volume $2v$ double that of half the quantity in a volume v; 2 is the entropy of an homogeneous gas mass in a volume v greater than the sum of the entropies of two such masses forming together the first quantity each in an equal volume v; 3 is the entropy of a mixture of 2 gases equal to the sum of the entropies of the two gases separately? In the entropy of BOLTZMANN the answer is every time affirmative.

If we consider $H = N\left(\log \frac{N}{v} + C\right)$, then in the 1st case $H_1 = N_1\left(\log \frac{N_1}{v} + C\right)$, so $2H_1 = 2N_1\left(\log \frac{N_1}{v} + C\right)$; further for the whole mass in the volume $2v$:

$$H = 2N_1\left(\log \frac{2N_1}{2v} + C\right) = 2N_1\left(\log \frac{N_1}{v} + C\right) = 2H_1 .$$

In the second case:

$$H_1 = N_1\left(\log \frac{N_1}{v} + C\right),\ H_2 = N_2\left(\log \frac{N_1}{v} + C\right),$$

so $H_1 + H_2 = N_1 \log N_1 + N_2 \log N_2 - (N_1 + N_2)(\log v + C)$, while $H = (N_1 + N_2) \log (N_1 + N_2) - (N_1 + N_2)(\log v + C)$, so that $H < H_1 + H_2$ or the entropy of the whole is greater than the sum of the entropies of the parts.

In the 3rd case the formula for H used here does not hold, but now BOLTZMANN puts here $H = H_1 + H_2$ *by definition*. For a mixture of two gases BOLTZMANN puts viz.:

$$H = \iint f \log f \, do \, d\omega + \iint f_1 \log f_1 \, do \, d\omega .$$

However, also the questions 1 and 2 might have been answered directly from this definition. $H = \iint f \log f \, do \, d\omega$ indicates, namely, that H of the whole $= \Sigma H$ of the parts; further we can always think the molecules divided into two parts with densities f_1 and f_2, so that $f = f_1 + f_2$,

$$(f_1 + f_2) \log (f_1 + f_2) < f_1 \log f_1 + f_2 \log f_2 ,$$

so that also $H < H_1 + H_2$. From this latter way of treatment appears at the same time that the three properties are also valid for the entropy of **Boltzmann** if the gas is *not* in the state of equilibrium.

To answer the same questions with regard to the entropy of **Gibbs** we consider the formula:

$$-\bar{\eta} = \frac{3}{2} N + \frac{3}{2} N \log (2\pi \, mT) + N \log v.$$

As to the first question for N_1 molecules in the volume v:

$$-\bar{\eta}_1 = \frac{3}{2} N_1 + \frac{3}{2} N_1 \log (2\pi \, mT) + N_1 \log v ,$$

so

$$-2\bar{\eta}_1 = 3N_1 + 3N_1 \log (2\pi \, mT) + 2N_1 \log v$$

and for $2N_1$ mol. in volume $2v$:

$$-\bar{\eta} = 3N_1 + 3N_1 \log (2\pi \, mT) + 2N_1 \log 2v ,$$

so that the entropy of the whole is *not* equal to the sum of the entropies of the parts. The *increase* in entropy (or free energy) of the whole, however, *is* always equal to the increase in entropy (or free energy) of the parts [1]).

As far as the second and third questions are concerned, we may directly take the general case of a mixture of two different gases and find then:

$$e^{-\frac{\psi}{T}} = (2\pi T)^{\frac{3N}{2}} \, m_1^{3\frac{N_1}{2}} \, m_2^{3\frac{N_2}{2}} \, v^N$$

from which:

$$-\frac{\psi}{T} = \frac{3N}{2} \log (2\pi T) + \frac{3N_1}{2} \log m_1 + \frac{3N_2}{2} \log m_2 + N \log v$$

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[1]) Accordingly the equation derived by Dr. L. S. **Ornstein** in his Thesis for the Doctorate: "Application of **Gibbs**'s Statistical Mechanics to molecular-theoretical problems", (Leiden 1908) p. 54:

$\sum_{1}^{k} (\psi_\varkappa - \psi_{0\varkappa}) = \psi - \psi_0$ states only that the *increase* in ψ of the joint elements forms the total increase in ψ of the whole. For the "zero-state", for which $\psi_{0\varkappa}$ and ψ_0 hold, viz. the state in which the potential energy $=0$, $\Sigma \, \psi_{0\varkappa} = \psi_0$ is by no means valid. It is exactly this "zero-state", that has been considered above.

and

$$-\bar{\eta} = \frac{3N}{2} + \frac{3N}{2} \log(2\pi T) + \frac{3N_1}{2} \log m_1 + \frac{3N_2}{3} \log m_2 + N \log v.$$

For the first substance alone we find:

$$-\bar{\eta}_1 = \frac{3N_1}{2} + \frac{3N_1}{2} \log(2\pi T) + \frac{3N_1}{2} \log m_1 + N_1 \log v,$$

for the second alone:

$$-\bar{\eta}_2 = \frac{3N_2}{2} + \frac{3N_2}{2} \log(2\pi T) + \frac{3N_2}{2} \log m_2 + N_2 \log v.$$

From this appears $-\bar{\eta} = -\bar{\eta}_1 + -\bar{\eta}_2$ or the entropy of the mixture is equal to the sum of the entropies of the gases forming the mixture, which now holds too if the component parts consist of the same gas. So there is no perfect harmony with thermodynamics: for this entropy GIBBS's paradox no longer holds.

That the $-\bar{\eta}$ of the whole volume is not equal to the $\Sigma -\bar{\eta}$ of the parts is a consequence of the fact that the extension in phase $v_1^{N_1} \times v_2^{N_2}$ is not equal to the extension $(v_1 + v_2)^{N_1 + N_2}$. In the total volume there are more possibilities of combination of place than when the volume has been divided into two separate parts. We may also say that BOLTZMANN's entropy just as in thermodynamics, may be divided with regard to the volume, GIBBS's entropy with regard to the molecules. If we compare the formulae :

$$H = N\left(\log \frac{N}{v} + C\right) \text{ and } \bar{\eta} = N(-\log v + C),$$

it appears that GIBBS's entropy can be brought into harmony with thermodynamics by augmenting $\bar{\eta}$ by $N \log N$ or $N(\log N + C')$. This may be done by multiplying the density e^{η} by $N^N . e^{-N}$ or $N!$ by approximation. So we should have to take for $\bar{\eta}$ the mean *log* of the density, not with respect to the *specific*, but with respect to the *generic* phases. [1])

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[1]) When I had written the above, I observed that the last remarks are not new. In the last sentence of his book GIBBS himself has already made the observation that we shall have to take $-\bar{\eta}_{gen}$ and not $-\bar{\eta}_{spec}$ as equivalent for the entropy, "except in the thermodynamics of bodies in which the number of molecules of the various kinds is constant." So it will always have to be done where the entropy of the whole is compared with that of the parts.

Nevertheless considering that GIBBS devotes so few words to the matter, I feel justified in not suppressing my remarks.

Physics. — *"On the law of molecular attraction for electrical double points."* By Prof. J. D. VAN DER WAALS JR. (Communicated by Prof. J. D. VAN DER WAALS).

Though Prof. M. REINGANUM has sometimes expressed the opinion that from the supposition that the molecules are electrical double points would follow that the molecular attraction decreases proportionally to $\frac{1}{r^4}$, he pointed out to me in a private letter that his deduction of the equation of state does not depend upon the accuracy of this opinion. In fact for every pair of molecules we have for the value of the potential energy

$$-\frac{m}{3r^3}\sqrt{3\cos^2\vartheta+1}\,.\cos\varphi$$

and so for the virial i. e. for $\frac{1}{2}rR$ — if r represents the line joining the molecules and R the component of the molecular force in the direction of this line —

$$\frac{m}{2r^4}\sqrt{3\cos^2\vartheta+1}\,.\cos\varphi,$$

so the ratio $\dfrac{\text{virial}}{\text{potential energy}}=\dfrac{3}{2}$.

As this ratio has the same value for each pair of molecules, it is also the ratio between the total virial of the attracting forces of all the molecules and the total potential energy. And it is this ratio which REINGANUM uses for his deduction of the equation of state.

So we see that this ratio has the same value as if the attraction decreased proportionally to $1/r^4$, though in reality the mean attraction decreases much more rapidly. If we wished to calculate this ratio by differentiating the value for the mean potential energy[1]) with respect to r, in order to find the force, and by multiplying this value by $^1/_2\,r$ in order to find the virial, we should find a value different from $^3/_2$. This is because we should not differentiate the *average* potential energy in order to find the *average* force, as I have l.c. erroneously written. In order to find the average force we must first find the force between two molecules by differentiating the potential energy with respect to r. Then we must multiply the result by:

$$e^{\frac{m^2\sqrt{3\cos^2\vartheta+1}\,.\cos\varphi}{3r^3t}}\;{}^1/_4\sin\varphi\,d\varphi\sin\vartheta\,d\vartheta.$$

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[1]) These proceedings XI, p. 132.

and integrate with respect to φ and ϑ. It is not allowed to change the order of these operations: to integrate first and to differentiate afterwards, as we should do if we calculated the attraction by differentiating E with respect to r. This is obvious from mathematical considerations, but it can also easily be shown from physical considerations. For we saw that the double points have yielded in a higher degree to the couples they exercise on one another, according as they have approached one another more closely.

If therefore we make a group of bipoles approach another bipole from a distance r_2 to a distance r_1, and if we want the axes of the bipoles, when they are at the distance r_1 to be orientated in the same way as may be expected from the laws of probability, then we must make the bipoles turn in the direction of the couples at the same time as they approach to the fixed double point. The loss of potential energy is therefore not equal to the work of the attracting forces but contains also the work of the couples and therefore we cannot find the average force by differentiating the average potential energy with respect to r.

The attraction of each pair of molecules is found by differentiating $-\frac{1}{3r^3}\sqrt{3\cos^2\vartheta+1}\,.\,\cos\varphi$ with respect to r, i.e. by multiplying this quantity by $-\frac{3}{r}$. Therefore we find also the value of the average force by multiplying the value of the average potential energy by $-\frac{3}{r}$; so we find:

$$K = t\sqrt{3}\,\frac{m^4}{9t^2r^7}\left\{\frac{p_1}{3!}+\frac{2m^2}{3^2t^2r^6}\frac{p_3}{5!}+\frac{3m^4}{3^4t^4r^{12}}\frac{p_5}{7!}+\dots\right\}$$

where the quantities p have the same signification as on p. 136 l.c.

It appears that the way in which the attraction depends on r is the same as I had indicated l. c., but that the coefficients have another value than we should find by differentiating E with respect to r.

Physics. — *"Contribution to the theory of binary mixtures"*. X. By Prof. J. D. van der Waals.

THE INTERSECTION OF THE CURVES $\frac{d^2\psi}{dx^2}=0$ AND $\frac{d^2\psi}{dv^2}=0$.

The points in which the two curves $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}$ intersect, lie of course in the unstable region. For it is required for the points of the spinodal line, the limit of the unstable region, that $\frac{d^2\psi}{dx^2}>0$ and $\frac{d^2\psi}{dv^2}>0$, and the product $\frac{d^2\psi}{dx^2}\frac{d^2\psi}{dv^2}=\left(\frac{d^2\psi}{dx\,dv}\right)^2$. Hence the use of the study of the way in which these two curves intersect, must not be looked for exclusively, nor even chiefly, in an indication for the course of the spinodal curve. It is, indeed, clear and has been repeatedly set forth in the previous papers that only in the cases in which there is intersection between the two curves, or when $\frac{d^2\psi}{dx^2}=0$ lies outside the curve $\frac{d^2\psi}{dv^2}=0$, the spinodal line deviates greatly from $\frac{d^2\psi}{dv^2}=0$; whereas, when $\frac{d^2\psi}{dx^2}=0$ lies entirely within $\frac{d^2\psi}{dv^2}=0$, the course of the spinodal line deviates little from the course of $\frac{d^2\psi}{dv^2}=0$. But above all the knowledge of the relative position of $\frac{d^2\psi}{dx^2}=0$ compared with $\frac{d^2\psi}{dv^2}=0$ seems of importance to me for the question whether for a given binary mixture three-phase-pressure is to be expected or not. And everything that can contribute to elucidate a matter of such practical importance, must necessarily be considered important. We shall again put $b=b_1(1-x)+b_2x$ also in this investigation, and so again disregard the influence of v on the value of b. So from a quantitative point of view our results may be very deficient. But on the other hand it has sufficiently appeared in our former investigation, in which the same approximation was used that the indication of the course of the phenomena obtained in such a way, is correct in the main.

So let us put:

$$\frac{d^2\psi}{dx^2}=MRT\left\{\frac{1}{x(-x)}+\frac{\left(\frac{db}{dx}\right)^2}{(v-b)}\right\}-\frac{\frac{d^2a}{dx^2}}{v}=0$$

and

$$\frac{d^2\psi}{dv^2}=\frac{MRT}{(v-b)^2}-\frac{2a}{v^3}=0\,.$$

When we eliminate T from these two equations, we get for the locus of the points of intersection of the two curves:

$$\frac{(v-b^2)}{x(1-x)}+\left(\frac{db}{dx}\right)^2=v^2\,\frac{\frac{d^2a}{dx^2}}{2a}\quad\ldots\ldots\ldots\ (a)$$

This locus, in which v occurs in the 2nd degree, and x in the 4th, may present a different shape, and in order to get a survey of the different shapes of this curve, we shall introduce some auxiliary quantities.

These auxiliary quantities will recommend themselves in the discussion of one of the special cases, and for this we choose the case that the whole locus is imaginary for all the values of x between 0 and 1. Let us for this purpose write the equation (a) in the following form:

$$v^2\left\{1-x\,(1-x)\,\frac{\frac{d^2a}{dx^2}}{2a}\right\}-2\,bv+\left\{b^2+x\,(1-x)\left(\frac{db}{dx}\right)^2\right\}=0\ \ .\ .\ (a')$$

For the case that this locus is imaginary

$$b^2<\left\{b^2+x\,(1-x)\left(\frac{db}{dx}\right)^2\right\}\left\{1-x\,(1-x)\,\frac{\frac{d^2a}{dx^2}}{2a}\right\}$$

or

$$0<x\,(1-x)\left\{\left(\frac{db}{dx}\right)^2-\frac{\frac{d^2a}{dx^2}}{2a}\,b^2-x\,(1-x)\left(\frac{db}{dx}\right)^2\frac{\frac{d^2a}{dx^2}}{2a}\right\}$$

or for x between 0 and 1:

$$0<\left\{\frac{\left(\frac{db}{dx}\right)^2}{b^2}-\frac{\frac{d^2a}{dx^2}}{2a}-x\,(1-x)\,\frac{\left(\frac{db}{dx}\right)^2}{b^2}\,\frac{\frac{d^2a}{dx^2}}{2a}\right\}$$

or for $\frac{d^2a}{dx^2}=2\,(a_1+a_2-2a_{12})$ positive, which we always assume in all our considerations:

$$0<\frac{a}{a_1+a_2-2a_{12}}-\frac{b^2}{\left(\frac{db}{dx}\right)^2}-x\,(1-x)\,.$$

If we write:

$$a = a_1 + 2\,(a_{12} - a_1)\,x + (a_1 + a_2 - 2a_{12})\,x^2$$

and

$$b^2 = b_1{}^2 + 2b_1\,\frac{db}{dx}\,x + \left(\frac{db}{dx}\right)^2 x^2,$$

the latter equation way also be written in the form

$$0 < \left[\frac{a_1}{a_1+a_2-2a_{12}} - \frac{b_1{}^2}{\left(\frac{db}{dx}\right)^2}\right] + x\left[\frac{2\,(a_{12}-a_1)}{a_1+a_2-2a_{12}} - \frac{2b_1}{\frac{db}{dx}} - 1\right] + x^2 \ldots (\beta)$$

If we demand that the locus be imaginary all over the width of the figure, so for all the values of x between 0 and 1, there are three conditions:

$$1^{\text{st}}\ \frac{a_1}{a_1+a_2-2a_{12}} > \frac{b_1{}^2}{(b_2-b_1)^2},\quad 2^{\text{nd}}\ \frac{a_2}{a_1+a_2-2a_1{}^2} > \frac{b_2{}^2}{(b_2-b_1)^2}$$

and a third condition which is still to be derived.

Let us write for this purpose $a_1 + a_2 - 2a_{12} = c$ and $b_2 = nb_1$, then $1^{\text{st}}\ \frac{a_1}{c} > \frac{1}{(n-1)^2}$, $2^{\text{nd}}\ \frac{a_2}{c} > \frac{n^2}{(n-1)^2}$ and when we introduce the auxiliary quantities ε_1 and ε_2, so that $\frac{a_1}{c} = \frac{1+\varepsilon_1}{(n-1)^2}$ and $\frac{a_2}{c} = \frac{n^2\,(1+\varepsilon_2)}{(n-1)^2}$ (ε_1 and ε_2 positive), we find from $2a_{12} = a_1 + a_2 - c$ or $\frac{2a_{12}}{2} = \frac{a_1}{c} + \frac{a_2}{c} - 1$

$$2\,\frac{a_{12}}{c} = \frac{1+\varepsilon_1}{(n-1)^2} + \frac{n^2 + n^2\,\varepsilon_2}{(n-1)^2} - 1$$

or

$$2\,\frac{a_{12}}{c} = \frac{2n + \varepsilon_1 + n^2\,\varepsilon_2}{(n-1)^2}.$$

So the condition that this locus be imaginary is that for all the values of x:

$$\frac{\varepsilon_1}{(n-1)^2} - x\left\{1 + \frac{\varepsilon_1 - n^2\varepsilon^2}{(n-1)^2}\right\} + x^2 > 0 \quad \ldots\ldots \quad (\beta')$$

or

$$\varepsilon_1 > 0 \quad \text{and} \quad \varepsilon_2 > 0 \quad \text{and} \quad 1 + \frac{\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2} < 2\,\frac{\sqrt{\varepsilon_1}}{n-1}$$

The last condition may be written more symmetrically in the form:

$$1 - 2\,\frac{\sqrt{\varepsilon_1}}{n-1} + \frac{\varepsilon_1}{(n-1)^2} < \frac{n^2\varepsilon_2}{(n-1)^2}$$

or

$$1-\frac{\sqrt{\varepsilon_1}}{n-1}<\frac{n\sqrt{\varepsilon_2}}{n-1}$$

or

$$\sqrt{\varepsilon_1}+n\sqrt{\varepsilon_2}>n-1\,.$$

So the condition ε_1 and $\varepsilon_2>0$ ensures that the locus does not take up the whole width from $x=0$ to $x=1$. For the locus not to exist at all the value of ε_1 and ε_2 must be such that:

$$\sqrt{\varepsilon_1}+n\sqrt{\varepsilon_2}>n-1\,.$$

If $\sqrt{\varepsilon_1}+n\sqrt{\varepsilon_2}=n-1$, the locus reduces to a single point. In this case:

$$\frac{\varepsilon_1}{(x-1)^2}-x\left\{1+\frac{\varepsilon_1-n^2\varepsilon_2}{(n-1)^2}\right\}+x^2=0.$$

The equation has two coinciding roots, i.e. $x=\dfrac{\sqrt{\varepsilon_1}}{n-1}$ or $1-x=\dfrac{n\sqrt{\varepsilon_2}}{n-1}$.

Perhaps these results might have been obtained in a more lucid way, if we had introduced the quantity $N=\dfrac{x}{1-x}$, instead of x into the equations (α) or (α'), so the number of molecules of the second substance present per molecule of the first substance in the binary mixture, which quantity must necessarily be positive. The condition that the two curves $\dfrac{d^2\psi}{dx^2}=0$ and $\dfrac{d^2\psi}{dv^2}=0$ do not intersect at any temperature assumes then the following form:

$$\frac{\varepsilon_1}{(n-1)^2}-N\left\{1-\frac{\varepsilon_1+n^2\varepsilon_2}{(n-1)^2}\right\}+\frac{\varepsilon_2 n^2}{(n-1)^2}N^2>0.\,.\quad .\quad .\quad (\gamma)$$

For $N=0$ and $N=\infty$ this condition is satisfied for positive ε_1 and ε_2. But for this equation to be satisfied for any arbitrary value of N it is required that:

$$1-\frac{\varepsilon_1+n^2\varepsilon_2}{(n-1)^2}<\sqrt{\frac{4\varepsilon_1 n^2\varepsilon_2}{(n-1)^2}}$$

or

$$1<\frac{\varepsilon_1+n^2\varepsilon_2+2\sqrt{n^2\varepsilon_1\varepsilon_2}}{(n-1)^2}$$

or

$$n-1<\sqrt{\varepsilon_1}+n\sqrt{\varepsilon_2}$$

If we construct the relation between ε_1 and ε_2 as a curve, taking ε_1 and ε_2 as coordinates, we get, for the case that the locus of the points of intersection contracts to a single point:

$$\left\{1 - \frac{\varepsilon_1 + n^2\varepsilon_2}{(n-1)^2}\right\}^2 = \frac{4n^2\varepsilon_1\varepsilon_2}{(n-1)^4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\gamma')$$

and so a parabola. We see from of (γ') that this parabola touches the ε_1 axis and the ε_2 axis in the points of intersection in which the straight line $\frac{\varepsilon_1 + n^2\varepsilon_2}{(n-1)^2} = 1$ intersects the axes. The equation of this

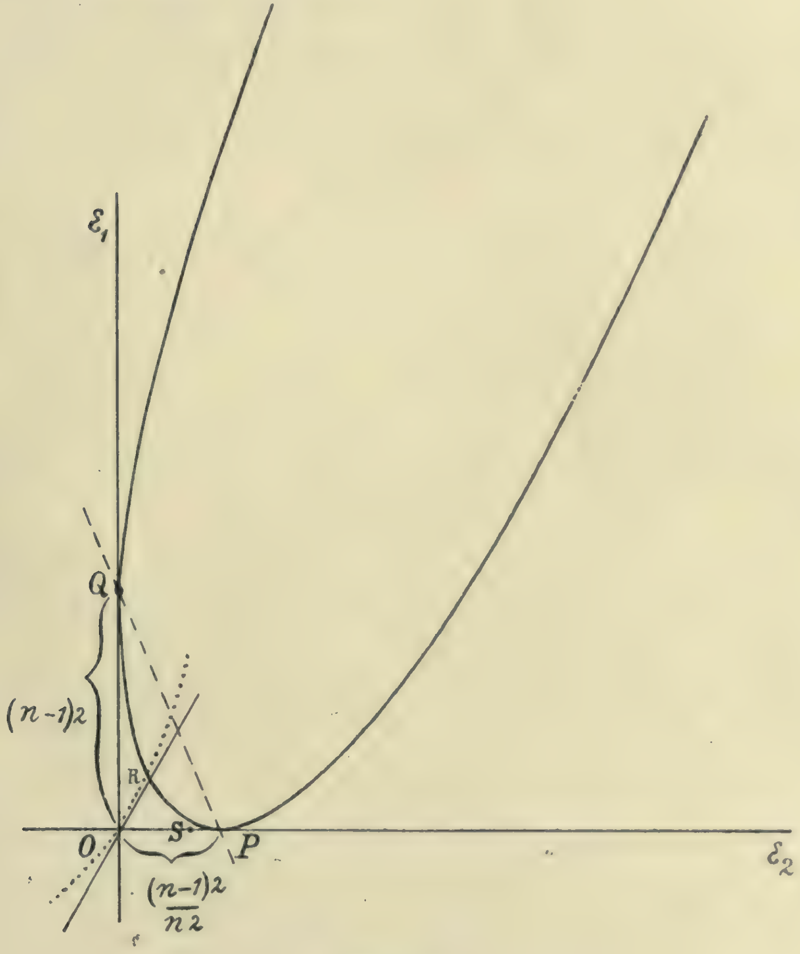

Fig. 36.

parabola may be written in the form $\frac{(\varepsilon_1 - n^2\varepsilon_2)^2}{(n-1)^4} - 2\,\frac{\varepsilon_1 + n^2\varepsilon_2}{(n-1)^2} + 1 = 0$, from which appears that the direction of the axis or of the diameters of this parabola is given by:

$$\frac{\varepsilon_1}{\varepsilon_2} = n^2 ,$$

the direction of the above straight line being given by:

$$\frac{\varepsilon_1}{\varepsilon_2} = -n^2.$$

So these two directions are symmetrical with respect to the axes mentioned. In fig. 36, in which the ε_2 axis has been drawn horizontally, the value of n, which is always larger than 1, is not supposed to be very large.

The calculation of the place of the top of the parabola may, among others, be made, by making use of the property that in the top the tangent to the parabola is normal to the direction of the diameter. So $\frac{d\varepsilon_1}{d\varepsilon_2} = n^2 \frac{\varepsilon_1 - n^2\varepsilon_2 + (n-1)^2}{\varepsilon_1 - n^2\varepsilon_2 - (n-1)^2} = -\frac{1}{n^2}$, from which follows that for the top $\varepsilon_1 - n^2\varepsilon_2 = -(n-1)^2 \frac{n^4-1}{n^4+1}$. This is the equation of the axis; it cuts the ε_2 axis in a point in which $\varepsilon_1 = 0$ and $\varepsilon_2 = OS = \frac{(n-1)^2}{n^2} \frac{n^4-1}{n^4+1}$. Hence $OS = OP \times \frac{n^4-1}{n^4+1}$. So for very small values of n also OS is small, but for larger value of n OS approaches to OP.

All the points inside this parabola give values for ε_1 and ε_2, for which equation (β) is satisfied; thus this equation reduces for all the points of the line PQ fig. 36 to:

$$\varepsilon_1 + \varepsilon_2 n^2 N^2 > 0$$

and for sets of values of ε_1 and ε_2, belonging to points lying within the parabola, there is, therefore, never intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$.

Summarizing we arrive at the following result. All the points in the positive quadrant of the ε_2, ε_1 axes of fig. 36, lying above the line PQ, represent sets of values of ε_1 and ε_2, for which (as N must always be positive) no intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ can take place. The points lying below PQ, but within the parabola, also represent such sets. The points below PQ, lying exactly on the parabola represent sets of ε_1 and ε_2, for which the locus of the points of intersection of the two curves mentioned reduces to a single point. And finally the points below PQ and below the parabola represent sets of values of ε_1 and ε_2 for which the two curves yield a locus of points of intersection. The point to which the locus of the points of intersection has contracted lies at a value of

$$N = \frac{x}{1-x} = \frac{1 - \frac{\varepsilon_1 + n^2\varepsilon_2}{(n-1)^2}}{\frac{n^2\varepsilon_2}{(n-1)^2}} = \frac{\sqrt{\varepsilon_1}}{n\sqrt{\varepsilon_2}}$$

, at which result we had already

arrived on p. 320, so near $x=1$, when $n^2\varepsilon_2$ is small compared with ε_1, and near $x=0$ when $n^2\varepsilon_2$ may be large compared with ε_1.

But now we have to consider the question whether such sets of values of ε_1 and ε_2 can actually occur for mixtures. As we do not know any rule as yet which indicates the value of a_{12} for given value of a_1 and a_2, we cannot give a perfectly decisive answer to this question. But we shall examine what may be derived about this from the rule which is of frequent application:

$$a_1a_2 > a_{12}^2$$

or

$$n^2(1+\varepsilon_1)(1+\varepsilon_2) > \left(n + \frac{\varepsilon_1 + n^2\varepsilon_2}{2}\right)^2$$

or

$$4n^2(1+\varepsilon_1)(1+\varepsilon_2) > [(1+\varepsilon_1) + n^2(1+\varepsilon_2) - (n-1)^2]^2$$

or

$$4\frac{n^2}{(n-1)^4}(1+\varepsilon_1)(1+\varepsilon_2) > \left[1 - \frac{(1+\varepsilon_1) + n^2(1+\varepsilon_2)}{(n-1)^2}\right]^2 \dots (\delta)$$

If we think for a moment the sign $>$ replaced by the sign $=$ the locus (δ) is perfectly equal to (γ), but with shifting of the two ordinates in the negative direction over an amount equal to -1. So if we draw two lines, one parallel to the horizontal ε_2 axis at a distance equal to -1, and one parallel to the vertical ε_1 axis at a distance -1, and if we construct the same parabola for these two lines, so that also the points P, Q, S are replaced by P', Q', S', and we have, accordingly, a line $P'Q'$, (δ) is satisfied for all points lying within this parabola.

For the points of the line $P'Q'$ the second member of (δ) is equal to 0 or $a_{12}=0$, and for the points lying below $P'Q'$ a_{12} would be negative. Accordingly these points will furnish no realizable sets of values of ε_1 and ε_2. But leaving this for the moment out of consideration, we may say that the series of points which the two parabolas mentioned have in common, fulfil the two requirements that they furnish sets of values of ε_1 and ε_2 which admit of no intersection of $\frac{d^2\psi}{dx^2}=0$ with $\frac{d^2\psi}{dv^2}=0$, and for which $a_1a_2 = a_{12}^2$. This holds equally for the points lying above the first parabola, but within the second. The second parabola enters the positive quadrant of the ε_1 and ε_2 coordinates in the origin, touches there a line $\varepsilon_1 - n\varepsilon_2 = 0$, and so cuts the first parabola in a point represented by R in fig. 36. The equation of the second parabola may, viz. be reduced to the form:

$$(\varepsilon_1 - n^2\varepsilon_2)^2 = 4n(n-1)(\varepsilon_1 - n\varepsilon_2).$$

But if, before drawing conclusions concerning the properties of the components of binary mixtures which admit of no intersection of $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}=0$, we consider the meaning of the condition $a_{12}^2 < a_1a_2$ more closely, it appears that the above remarks should be greatly restricted. Up to now we have been able to draw the conclusion that $a_{12}^2 = a_1a_2$ leads to a relation between ε_1 and ε_2 which is graphically represented by what we have called the second parabola, and we have further observed that the condition $a_{12} < a_1a_2$ leads to values of ε_1 and ε_2 belonging to points lying within that parabola. According to this view, however, also points lying at infinite distance on or in the neighbourhood of the axis of the second parabola, would furnish sets of values for ε_1 and ε_2 which might be considered to properly satisfy the condition $\frac{a_{12}^2}{a_1a_2} < 1$. For these points a_{12}^2 is indeed $< a_1a_2$, but as well a_1 as a_2 and a_{12} would be infinitely large for these points, and the ratio of $\frac{a_{12}^2}{a_1a_2}$ for these points is equal to 1. We get a more accurate limitation of possible values of ε_1 and ε_2 by putting $a_{12}^2 = l^2a_1a_2$ with the condition $l^2 < 1$. So let us put:

$$4l^2n^2(1+\varepsilon_1)(1+\varepsilon_2) = (2n+\varepsilon_1+n^2\varepsilon_2)^2 . \quad . \quad . \quad . \quad (d')$$

or

$$\varepsilon_1^2 - 2n^2\varepsilon_1\varepsilon_2(2l^2-1) + n^4\varepsilon_2^2 = 4n\{\varepsilon_1(l^2n-1) - n\varepsilon_2(n-l) - n(1-l^2)\}$$

This equation represents an ellipse for $l^2 < 1$; for $l^2 = 1$ a parabola and for $l^2 > 1$ a hyperbola. From the form (d') we see that this locus touches the lines $\varepsilon_1 = -1$ and $\varepsilon_2 = -1$ in the points in which these lines are intersected by the same line $P'Q'$, which has been mentioned above in the description of the second parabola. If we now again ask if sets of values of ε_1 and ε_2 are possible belonging to components the binary mixture of which does not admit of intersection of $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}=0$, we notice in the first place that then the ellipse (d') must intersect the first parabola and the line PQ.

Now, dependent on the value of l^2 in connection with the value of n it is possible that the ellipse remains entirely restricted to negative values of ε_2, in which case intersection with the first parabola is out of the question.

This takes place when the relation between l^2 and n is such that the equation: $4l^2n^2(1+\varepsilon_1) = (2n+\varepsilon_1)^2$ yields equal or imaginary values for ε_1, and so when:

$$l^2n^2 \leqq 2n - 1$$

holds; for small value of n, e. g. $n = 1{,}5$, l^2 would have to be $< \frac{8}{9}$, which has certainly been found in observations; but for larger values of n, e.g. $n = 5$, l^2 would have to be $< \frac{9}{25}$ which will, most likely, not be the case. So if n is large for a not too small value of l^2, the ellipse (d') will also possess points for which ε_1 and ε_2 is positive, and the possibility that it intersects the 1st parabola, is not excluded. At given l^2 we might find the limit for the value of n, at which it is still possible that $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ do not intersect, by determining the relation which must exist between l^2 and n for the ellipse to touch the first parabola. But this would lead to lengthy calculations, which we shall omit here. We will, however, examine more closely some properties of the ellipse.

1. Determination of the centre.

From $f'(\varepsilon_1) = 0$ and $f'(\varepsilon_2) = 0$ or $2n + \varepsilon_1 + n^2\varepsilon_2 = 2l^2n^2(1 + \varepsilon_2)$ and $2n + \varepsilon_1 + n^2\varepsilon_2 = 2l^2(1 + \varepsilon_1)$ follows $(1 + \varepsilon_1)_M = n^2(1 + \varepsilon_2)_M$, from which follows that the line $O'M$ (fig. 37) makes an angle

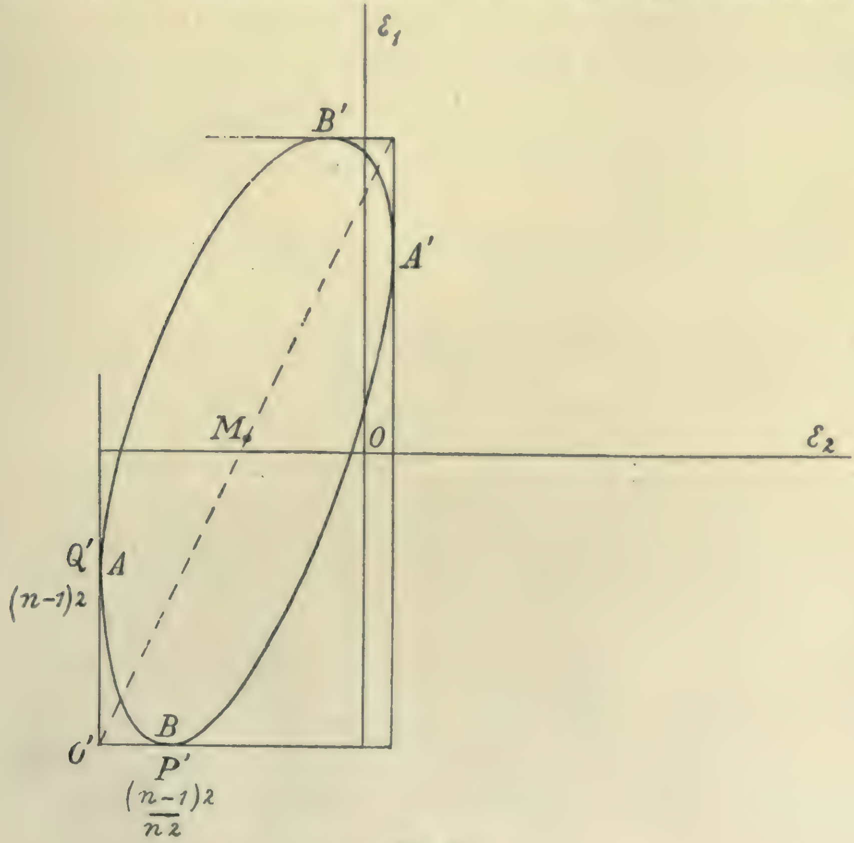

Fig. 37.

with the ε_2 axis, the tangent of which is equal to n^2, hence $O'M$ is parallel to the axis of the first parabola. For the coordinates of the centre we find:

$$(1+\varepsilon_1)_M = \frac{(n-1)^2}{2(1-l^2)} \text{ and } (1+\varepsilon_2)_M = \frac{(n-1)^2}{2n^2\,(1-l^2)}\,.$$

2. Highest and lowest point.

For these points $f'\varepsilon_2 = 0$ or

$$-(n-1)^2 + (1+\varepsilon_1) + n^2\,(1+\varepsilon_2) = 2l^2\,(1+\varepsilon_1)$$

and so $4l^2n^2\,(1+\varepsilon_1)\,(1+\varepsilon_2) = 4l^4\,(1+\varepsilon_1)^2$.

Hence $1+\varepsilon_1 = 0$ for the point B and $(1+\varepsilon_1) = \frac{n^2}{l^2}\,(1+\varepsilon_2)$ for the point B'; from this follows for B' the value $(1+\varepsilon_1)_{B'} = \frac{(n-1)^2}{1-l^2}$ and $(1+\varepsilon_2)_{B'} = \frac{l^2}{1-l^2}\,\frac{(n-1)^2}{n^2}$ and for B is $1+\varepsilon = \frac{(n-1)^2}{n^2}$.

3. The points A and A'.

For these points $f'\varepsilon_1 = 0$ or

$$-(n-1)^2 + (1+\varepsilon_1) + n^2\,(1+\varepsilon_2) = 2l^2n^2\,(1+\varepsilon_2)$$

and so $4l^4n^4\,(1+\varepsilon_2)^2 = 4l^2n^2\,(1+\varepsilon_1)\,(1+\varepsilon_2)$.

Hence for A $1+\varepsilon_2 = 0$ and $1+\varepsilon_1 = (n-1)^2$ and for A' holds $(1+\varepsilon_1) = l^2n^2\,(1+\varepsilon_2)$ or $(1+\varepsilon_2)_{A} = \frac{(n-1)^2}{n^2}\,\frac{1}{1-l^2}$ and:

$$(1+\varepsilon_1)_{A'} = \frac{l^2}{1-l^2}\,(n-1)^2\,.$$

4. The points of intersection with the ε_2 axis.

From $(2n + n^2\varepsilon_2)^2 = 4n^2l^2\,(1+\varepsilon_2)$ follows:

$$\varepsilon_2 = \frac{-2\,(n-l^2) \pm l\sqrt{(n-1)^2 - (1-l^2)}}{n^2}\,.$$

So while $1-l^2 < (n-1)^2$ there are two points of intersection with the ε_2 axis both on the negative side of the origin. For $l^2 = 1$ one of the points of intersection lies in the origin, and the other point of intersection at $\varepsilon_2 = -4\frac{n-1}{n^2}$, which value $= -1$ for $n = 2$, and for all other values of n not so large negative. For $1-l^2 = (2-1)^2$ the two points of intersection with the ε_2 axis coincide, and for $1-l^2 > (n-1)^2$ they are imaginary; then the whole ellipse has descended below the horizontal axis. For the case that n is but little larger than 1, this circumstance is to be expected; then only negative values of ε_1 and ε_2 exist.

5. The intersection with the ε_1 axis.
From $(2n + \varepsilon_1)^2 = 4n^2 l^2 (1 + \varepsilon_1)$ follows:

$$\varepsilon_1 = 2n\,(nl^2 - 1) \pm 2nl^2 \sqrt{\{n^2 l^2 - 2n + 1\}}.$$

For $l^2 = 1$, we get $\varepsilon_1 = 0$ and $\varepsilon_1 = 4n\,(n - 1)$. For $l^2 < 1$ these values approach each other, and they coincide for $l^2 = \frac{2n-1}{n^2}$ as was stated above. For $l^2 < \frac{2n-1}{n^2}$ or $1 - l^2 > \frac{(n-1)^2}{n^2}$ positive values of ε_1 no longer occur. For $l^2 = \frac{3}{4}$ e.g., the ellipse will just touch the ε_1 axis for $n = 2$, and that in a point for which $\varepsilon_1 = 2$; but for smaller value of n the ellipse does not cut the ε_1 axis; for larger value of n, on the other hand, it does.

6. The intersection with the line PQ of fig. 36.
If in:

$$(2n + \varepsilon_1 + n^2 \varepsilon_2)^2 = 4n^2 l^2 (1 + \varepsilon_1)(1 + \varepsilon_2)$$

we substitute the value $\varepsilon_1 + n^2 \varepsilon_2 = (n - 1)^2$, we find for the determination of ε_2 the equation:

$$n^2 \varepsilon_2^{\,2} + 2\,(n-1)\varepsilon_2 + \frac{(n^2 + 1)^2}{4n^2 l^2} - [1 + (n-1)^2] = 0.$$

When $l^2 < \frac{(n^2 + 1)^2}{4n^2\,[1 + (n-1)^2]}$ the two values of ε_2 are negative. If l^2 is greater, a point of intersection is found at positive value of ε_2; for l^2 just equal to the given value the ellipse passes exactly through the point Q, and the same relation exists between l^2 and n, as is also found when we substitute the value $(n-1)^2$ for ε_1 in the equation of 5.

While one of the values of ε_2 is positive the ellipse intersects not only the line PQ, but also the first parabola. For smaller value of l^2 or larger of n, the line PQ is no longer intersected in the positive quadrant; intersection of the ellipse with the first parabola will, indeed, be still possible, till the two points of intersection coincide with further decrease of l^2. Then the ellipse touches the parabola, and the possibility that $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ no longer intersect, vanishes.

7. Another form for the equation of the ellipse.

Most of the above results may be obtained by considering that the equation of the ellipse may also be written in the form:

$$\left\{(1+\varepsilon_1)+n^2(1+\varepsilon_2)-\frac{1+l^2}{1-l^2}(n-1)^2\right\}^2=4n^2l^2\left\{1+\varepsilon_1-\frac{(n-1)^2}{1-l^2}\right\}$$
$$\left\{1+\varepsilon_2-\frac{(n-1)^2}{n^2}\,\frac{1}{1-l^2}\right\}.$$

The first member put equal to 0 is the equation of the line $A'B'$, and the factors of the second member put equal to 0 are the equations of tangents to the ellipse in the points B' and A'.

If the ellipse intersects the first parabola, and so also twice the ε_1 axis, and if therefore part of the ellipse lies within the first parabola, then there is a continual series of points which yield sets of values of ε_1 and ε_2 for which no three-phase-pressure is to be expected. This series of points begins where the ellipse cuts the first parabola in the 1st or lowest point, and terminates either in the second point of intersection or in the ε_1 axis. In the latter case when the second point of intersection with the ε_1 axis lies higher than $(n-1)^2$.

8. Ratio of the critical temperatures of the components.

For a point of the ellipse is $\frac{a_1}{c}=\frac{1+\varepsilon_1}{(n-1)^2}$ and $\frac{a_2}{c}=\frac{n^2(1+\varepsilon_2)}{(n-1)^2}$, and so $\frac{T_{k_2}}{T_{k_1}}=\frac{n(1+\varepsilon_2)}{(1+\varepsilon_1)}$. If from the point O' ($\varepsilon_1=-1$ and $\varepsilon_1=-1$) we draw a line to such a point, and if we put the angle which this line makes with the ε_2 axis equal to φ, then $\frac{1+\varepsilon_1}{1+\varepsilon_2}=tg\,\varphi$, and so also $\frac{T_{k_2}}{T_{k_1}}=n\cot\varphi$ or $tg\,\varphi=n\frac{T_{k_1}}{T_{k_2}}$. If we put the question whether all the points of the ellipse can occur, we notice first of all that the condition $a_{12}>0$ already excludes the points lying below the line $P'Q$. Let the ellipse be inclosed in a rectangle, the sides of which are parallel to the axes, let us draw the diagonal through the centre for which $tg\,\varphi=n^2$ from the point O' ($\varepsilon_1=-1$ and $\varepsilon_2=-1$). This diagonal cuts the ellipse in a point that belongs to $\frac{T_{k_2}}{T_{k_1}}=\frac{1}{n}$. For all the points of the ellipse lying right of this point, $tg\,\varphi>n^2$, and so $\frac{T_{k_2}}{T_{k_1}}<\frac{1}{n}$. Thus we should have $\frac{T_{k_2}}{T_{k_1}}=\frac{l^2}{n}$ for the highest point of the ellipse. We cannot assert with any certainty that such cases do not occur. Substances with larger molecules have not a necessarily higher T_k, and that the critical temperature can be lower with $n>1$

we have assumed as possible among others in the course of the isobars.

When we take into account mixtures of water and other substances, we find this frequently to be the case. Thus for water and ether n is about 5 and $(T_k)_{ether}$ = about $\frac{3}{4}(T_k)_{water}$. For water and CO_2 $n = 2{,}5$ and $\frac{T_{k_2}}{T_{k_1}} = \frac{304}{638}$. For water and nitrogen $n = 1{,}6$ and $\frac{T_{k_2}}{T_{k_1}}$ much smaller than $\frac{1}{n}$. But it still remains an open question in how far our theory may be applied in unmodified form for mixtures of which one of the components is *water*, a substance which behaves so abnormally. In any case it is only by way of exception that points of the ellipse lying on the left of the diagonal, are of practical importance. If we now proceed to consider points right of the diagonal we mention in the first place the point in which the ellipse is cut by a line from C, and for which $tg\,\varphi = n$. For this point $\frac{T_{k_2}}{T_{k_1}} = 1$. For all the points for which $tg\,\varphi$ lies between n^2 and n $T_{k_2} < T_{k_1}$. But for points for which $tg\,\varphi < n$, $T_{k_2} > T_{k_1}$. So mixtures of substances for which the substance with the larger molecule has also the higher critical temperature are represented by those points of the ellipse for which $tg\,\varphi < n$, whereas, if $tg\,\varphi = 1$, we have the case that the critical pressures are the same. For this value of $\frac{p_{k_2}}{p_{k_1}}$ is equal to $\frac{1+\varepsilon_2}{1+\varepsilon_1}$. So the points for which $\frac{1+\varepsilon_1}{1+\varepsilon_2} < 1$ represent mixtures for which the substance with the larger molecule has not only higher critical temperature, but also higher critical pressure. Such lines intersect the ellipse in points in which both ε_1 and ε_2 is negative, and as it is required for non-intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ that these quantities are positive, and lie even beyond the line PQ, the rule would follow that for mixtures of substances for which the substance with the larger molecule has the greater critical pressure three-phase-pressure must occur. If experience should refute this, i.e. if it should appear that for mixtures of such substances absence of three-phase-pressure can be found, we should be induced to put the question: Is perhaps in some cases

$$a_{12}^2 > a_1 a_2$$

possible; then in the equation (σ) viz.:

$$4l^2 n^2 (1+\varepsilon_1)(1+\varepsilon_2) = \{2n+\varepsilon_1+n^2\varepsilon_2\}^2$$

the quantity l^2 is >1, and this equation represents a hyperbola.

For $l^2>1$ the two points of intersection with the ε_2 axis lie on the negative side of the origin. For $l^2=1$ one of the points of intersection has got into the point O, and for $l^2>1$ one of the points of intersection lies on the righthand side of O, so at a value of ε_2 which is positive. The branch of the hyperbola passing through this point, then intersects the first parabola and the line PQ, or only the first parabola; a line $\frac{1+\varepsilon_1}{1+\varepsilon_2}<1$ can then cut the hyperbola in points for which ε_1 and ε_2 are positive, and then absence of three-phase-pressure may again be expected.

But let us return to the examination of the equation (a') after our digression. Till now we have discussed the condition on which this equation has no real root. Let us now pass to other possible cases. The roots of this equation have the form:

$$\frac{v}{b} = \frac{1 \pm \sqrt{\left\{1-\left[1-x(1-x)\frac{c}{a}\right]\left[1+x(1-x)\frac{\left(\frac{db}{dx}\right)}{b^2}\right]\right\}}}{1-x(1-x)\frac{c}{a}}$$

or

$$\frac{v}{b} = \frac{1 \pm \sqrt{x(1-x)\frac{c}{a}\frac{\left(\frac{db}{dx}\right)^2}{b^2}}\sqrt{-\frac{\varepsilon_1}{(n-1)^2}+x\frac{\varepsilon_1-n^2\varepsilon_2}{(n-1)^2}+x(1-x)}}{1-x(1-x)\frac{c}{a}}$$

We shall continue to suppose the denominator to be positive. For $x=0$ the expression under the radical sign is equal to $-\frac{\varepsilon_1}{(n-1)^2}$ and for $x=1$ equal to $-\frac{n^2\varepsilon_2}{(n-1)^2}$, and for these values $\frac{v}{b}$ is, therefore, imaginary for positive ε_1 and ε_2. Now we put $\sqrt{\varepsilon_1}+n\sqrt{\varepsilon_2}>n-1$ before; this supposition implies that $\frac{v}{b}$ is imaginary all over the width from $x=0$ to $x=1$. Let us now put $\sqrt{\varepsilon_1}+n\sqrt{\varepsilon_2}<n-1$.

Then the equation $-\frac{\varepsilon_1}{(n-1)^2}+x\frac{\varepsilon_1-n^2\varepsilon_2}{(n-1)^2}-x(1-x)=0$ has two roots for x between 0 and 1. For these definite values of x $\frac{v}{b}$ has two equal values. For x outside these values $\frac{v}{b}$ is imaginary, and within these limits two positive values of $\frac{v}{b} > 1$ satisfy. That $\frac{v}{b} > 1$ or $\frac{v-b}{b}$ is positive may among others be seen when we have developed the equation (α) as quadratic equation in $(v-b)$. The two real values of $\frac{v-b}{b}$ are both positive, if $\frac{\left(\frac{db}{dx}\right)^2}{b^2} > \frac{c}{a}$; and the equation in x requires that this condition is fulfilled for real values of $\frac{v}{b}$. From this follows that if the conditions $\varepsilon_1 > 0$, $\varepsilon_2 > 0$ and $\sqrt{\varepsilon_1} + n\sqrt{\varepsilon^2} < n-1$ are fulfilled the locus of the points of intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ is a closed figure. The limiting values for $N = \frac{x}{1-x}$ have been given (see formula (γ)) by:

$$\frac{\varepsilon^1}{(n-1)^2} - N\left\{1 - \frac{\varepsilon^1 + n^2\varepsilon_2}{(n-1)^2}\right\} + N^2\frac{n^2\varepsilon_2}{(n-1)^2} = 0.$$

For these values of x, the volumes for a given value of x have coincided, and are equal to $\frac{b}{1-x(1-x)\frac{c}{a}}$. The existence of such a closed figure with volumes larger than b means that at exceedingly low temperature the two curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ do not intersect. Not before a certain value of T e.g. T_1 these two meet. At the lower temperatures the whole curve $\frac{d^2\psi}{dx^2} = 0$ lies in the space where $\frac{d^2\psi}{dv^2}$ is negative. At T_1 the branch of the small volumes of $\frac{d^2\psi}{dv^2} = 0$ has overtaken the branch of the small volumes of $\frac{d^2\psi}{dx^2} = 0$. At $T > T_1$ part of $\frac{d^2\psi}{dx^2} = 0$ lies in the region where $\frac{d^2\psi}{dv^2}$ is positive. But with further rise of the temperature a change is brought about in the relative movement of the two curves inter se, and at certain temperature equal to T_2 the branches of the small volumes of the two curves meet again; and at still higher temperature $\frac{d^2\psi}{dx^2} = 0$ lies again entirely within $\frac{d^2\psi}{dv^2} = 0$. Then three-phase-pressure is to be expected between two temperatures, whose values though not coinciding with T_1 and T_2, are yet in close connection with these values. But for this I refer to previous papers.

The two values of x, between which the locus of the points of intersection $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ is contained, lie in general not symmetrically with respect to $x = 0$ and $x = 1$. Let these values be denoted by x_1 and x_2, then:

$$x_1 + x_2 = 1 + \frac{\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2}$$

or if the value of x, which lies halfway between them is called x_m:

$$2x_m = 1 + \frac{\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2} .$$

So if $\varepsilon_1 > n^2\varepsilon_2$, then $x_m > \frac{1}{2}$ and vice versa. This remark may contribute to the solution of the question whether for mixtures for which three-phase-pressure exists between two temperatures T_1 and T_2, the quantity $l^2 > 1$ or < 1. If $l^2 < 1$, and if, therefore, the points for which ε_1 and ε_2 are the coordinates, can but lie on an ellipse which can only enter the space between the ε_1 and ε_2 axis and the first parabola in a point $\varepsilon_1 > 0$ and $\varepsilon_2 = 0$, then $x_m > \frac{1}{2}$ may be expected. On the other hand if $l^2 > 1$, and the considered points lie on a hyperbola, $\varepsilon_2 > 0$ and $\varepsilon_1 < n^2\varepsilon_2$ is to be expected. Then the discussed locus lies on the side of the component of the smallest size of the molecules — which occurs for mixtures of ethane and alcohols. For the case $\varepsilon_1 = 0$ and $n^2\varepsilon_2 > 0$, $x_1 = 0$ and $x_2 = 1 - \frac{n^2\varepsilon_2}{(n-1)^2}$. But $x_1 = 0$ for $v - b = 0$, from which follows at the same time $T_1 = 0$, so there is in this case three-phase-pressure at all temperatures below T_2. In the same way the value of T_1 would be equal to zero for $\varepsilon_2 = 0$ and $\varepsilon_1 > 0$.

In all this it must not be overlooked that though the presence or absence of three-phase-pressure is, indeed, closely connected with the presence or absence of the locus of the points of intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$, there are differences to be expected in the particulars. Thus the temperatures for the limits between which three-phase-pressure can be observed, are not the same as we have denoted by T_1 and T_2. First of all on account of the theoretical existence of *hidden* three-phase-pressure; but also because the presence or absence of a hidden plaitpoint does not coincide with the intersection or non-intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$. Moreover the existence of the liquid state is also assumed here for all temperatures, however low. The occurrence of the solid state may, of course, be a hindrance for the observation of what we have called the temperature T_1. Thus in mixtures of water and phenol an upmost temperature limit has been found for three-phase-pressure; but it is still an open question whether there also exists a lowest temperature, higher than the absolute zero point.

(*To be continued*)

Physics. — "*On the measurement of very low temperatures. XXI. On the standardizing of temperatures by means of boiling points of pure substances. The determination of the vapour pressure of oxygen at three temperatures.*" By Dr. H. KAMERLINGH ONNES and Dr. C. BRAAK. Communication N°. 107^a from the physical laboratory at Leiden.

(Communicated in the meeting of May 30, 1908).

§ 1. *Introduction.* In a preceding Communication N°. 101^a (Dec. '07) we have spoken of the desirability of determining once for all certain temperatures by means of boiling point apparatus, because the points of the temperature scale thus fixed have the advantage over those fixed with resistance thermometers and thermo-elements that they do not depend on the durability of special apparatus and they facilitate comparisons between thermometers in different laboratories.

This Communication treats of a number of determinations with oxygen: *a.* a little above and a little below the normal boiling point from which the latter could be derived; *b.* at 366 and 516 mm. mercury pressure which may serve to give information about the further course of the vapour pressure curve.

After some preliminary determinations we have constructed two apparatus of different dimensions, in each of which different quantities of gas could be successively condensed. Thus we have obtained two series of independent determinations; at the same time the purity of the gas could be tested.

§ 2 *The measuring apparatus.* (See Pl. I).

In the vapour pressure apparatus of the small pattern A about 120 cc. gas can be condensed, in the large pattern B about 1 Liter. Pattern A consists of a bulb a of 0.5 cc. with a glass stem b, connected to a manometer with a steel capillary c. The manometer consists of two tubes $m_1 m_2$ of 2 cm. bore filled with mercury; they are connected by an india rubber tube. An air-trap d prevents impurities from coming into the gas. The glass stem is moreover surrounded by a copper cylinder e and a glass jacket f by means of which heat is conducted from above, thus preventing the temperature at any part of the apparatus from falling below that of the bulb which is placed in the cryostat at the place where the temperature is measured. By pressing the mercury higher up or lower down one can condense different quantities of gas successively.

The construction of pattern B differs a little from that of A; this is especially in order to avoid the apparatus becoming difficult to handle because a too large quantity of mercury would be required. The manometer $m_1 m_2$ consists of a U-tube of glass of which the two limbs are separated by a glass cock k_1. This U-tube is blown on to another $d_1 d_2$ which contains the gas. The two limbs of the latter are cylinders of 70 c.m. length and 0.5 liter contents separated by a cock k_2. The limb d_1 connected to the manometer is fixed at its upper end to the steel capillary c which is connected with the bulb a. The limb d_2 carries a glass cock k_3, through which the apparatus is filled. The reservoir is filled to 1 atm. excess of pressure with gas. By first shutting k_2 and then opening it we can condense first the gas of d_1 which is under an excess of pressure, then also that of d_2.

A enables us to judge of the purity of the gas when we investigate in how far the vapour pressure measured depends on the fraction of the quantity of gas already condensed. By means of B, where the quantity of condensed gas always amounts to the same portion of the total quantity, we can determine in how far the vapour pressure is independent of the increase or decrease of the quantity of the condensed gas itself.

The oxygen is prepared from potassium permanganate through heating. After it has been carefully purified and dried over a KOH-solution and P_2O_5 the gas is condensed in a bulb immersed in liquid air. Then the liquid air is removed and the apparatus are filled with the evaporated gas.

The pressure was read with a cathetometer; this does not require a very high degree of accuracy because of the great variability of the vapour pressure with the temperature. The atmospheric pressure on the mercury in the open manometer was read on an aneroid barometer which we occasionally compared with a mercury barometer.

§ 3. *The determination of temperature and the degree of accuracy.*

For measuring the temperature we have used for the determinations in the neighbourhood of the boiling point of oxygen the resistance thermometer Pt'_I which has been compared 1) (comp. Comms. N°. 95^c Sept. '06 and N°. 101^a Dec. '07) over a large range with the hydrogen thermometer of Comm. N°. 95^e (Oct. '06) which we shall call B_{III}; for — 182° this was done on March 25th 1907 (comp. Comm. N°. 101^a table I). Some calibrations have afterwards been made, which together with those just named are given in table II. This table also contains the results of an indirect comparison of Pt'_I with another hydrogen thermometer, which we call T_4 and which was used in an investigation of Dr. FEUSTEL and one of us (K. O.) with a differential thermometer helium-hydrogen, which investigation will soon be published.

In connection with § 4 of Comm. N°. 101^a we have also given in table I the results of 4 comparisons between two resistance thermometers Pt'_I and Pt''_d 3) at about — 183° C. and — 217° C.

TABLE I. Comparison between Pt'_I and Pt'_d.

Date	Pt'_I	Pt'_d	Pt'_I and Pt'_d in degrees
22 June '07	34.267	18.565 3)	0°.000
18 Dec. '07	34.359	18.609	
24 June '07	14.761	9.1483 3)	0°.007
19 Dec. '07	14.824	9.1793	

For the measurements on 18th and 19th Dec. '07 B_{III}, Pt'_I and

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1) $W_{PtI} = 1.01806\ W_{Pt'I}$ (comp. § 2 of Comm. N°. 101^a Dec. 1907).

2) This resistance thermometer is the same as the one which in Comm. N°. 99^b (Sept. '07) is called Pt'_d. Afterwards it has broken in the middle, and consequently the resistance was diminished to half its value (Pt'_d). Here it is indicated with two accents because it has then undergone a small reparation owing to which $Pt''_d = 1.00073\ Pt'_d$ at 0°.

3) This value has been reduced with the factor of the preceding footnote.

Pt''_d were placed in the cryostat. Thus we simultaneously obtained the results relating to them of the tables I and II. Those of the second part of table II are derived from a comparison between Pt''_d and T_4. The resistances observed were reduced with the factor 1.00073 (cf. the footnote on the preceding page), giving 18.560 and 18.398 Ω. These have been reduced with the data of table I to Pt'_I. This yields the values of the third column.

The calibration of T_4 agrees satisfactorily with that of B_{III}. The mean of the deviations for the two former and the two latter data differs from table II by 0.022 Ω which corresponds to 0°.038. This small difference between the readings of two entirely different gas thermometers satisfactorily confirms the exactness of the limit of accuracy derived formerly (Comm. N°. 95^e) and enhances the reliability of the other preceding determinations of temperature.

TABLE II. Comparison of the resistance thermometer Pt'_I with the hydrogen thermometers B_{III} and T_4.

Date	Temperature according to the hydrogen thermom. B_{III}	Resistance in Ω	$O_{Pt'_I} - C_{A_I}$
Comparison with B_{III}			
25 March '07	— 182°.352	34.492	— 0.008
18 Dec. '07	— 182°.595	34.359	— 0.000
17 Febr. '08	— 186°.590	32.027	— 0.019
18 Febr. '08	— 189°.509	30 332	— 0.041
19 Dec. '07	— 216°.840	14.824	+ 0.031
Comparison with T_4			
30 Nov. '07	— 182°.736 [1])	34.257	— 0.021
3 Dec. '07	— 183°.302 [1])	23.919	— 0.031

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[1]) The hydrogen thermometer temperatures are calculated on the scale of Comm. N°. 95^e (Oct. '06). As the zero pressure amounted to about 1360 mm. we have accordingly accepted for the coefficient of pressure variation 0.0036629, derived from the coefficient of pressure variation of Comm. N°. 60 (Sept. 1900) (0.0036627 for 1100 mm. zero pressure). We have also applied a correction according to the difference of the correction to the absolute scale for 1360 and 1100 mm. zero pressure.

The tables I and II also give new data about the accuracy of the readings of the resistance and of the gas thermometer[1]). According to table I the error of the resistance remains below 0.°01. As to the readings of the gas thermometer, the first two data of table II inter se yield a difference smaller than 0.°02. With the difference + 0.031 Ω at — 217° correspond + 0,028 and + 0.016 of table II in Comm. N°. 95^c and table I in Comm. N°. 101^a. This also agrees with the accuracy of 0.°02 derived in § 7 of Comm. N°. 95^e. This seems not to be the case for the value of 18 Febr. '08 which deviates rather much from the formula. It will depend on later determinations what part of this deviation must be ascribed to the formula *AI*.

§ 4. *The vapour pressure determinations in the neighbourhood of the boiling point of oxygen.*

We have used the cryostat described in Comm. N°. 94^f (Pl. V) Sept. 1906). The temperature was determined and regulated with the resistance Pt'_I placed in the bath. The deviations of the galvanometer were so small that no correction was required for it. In the apparatus *A* the mercury was raised successively in the lower and the upper end of the manometer m_1, in *B* first the gas of one reservoir was condensed, afterwards of the two reservoirs. This is indicated in the following table with "little" and "much". Table III contains a determination at a small excess of pressure, another at a pressure of a little below 760 m.m. and a determination for control also at an excess of pressure. The pressure is reduced to 0° C. The last column contains the deviations from the mean for each series.

The resistances of the thermometer read on the WHEATSTONE bridge were for the three series respectively:

34.433 , 34.098 and 34.433 Ω.

If we compare the results obtained with the condensation of a little quantity of gas with those with the condensation of a large quantity we cannot find any systematical deviations, which speaks for the purity of the gas used. In case impurities should occur their influence on the vapour pressure derived with the smaller condensation is sure to be less than the influence on the difference just mentioned. It may therefore be neglected.

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[1]) Comp. Comms. No. 95^c, 95^c and 101^a.

TABLE III. Vapour pressure of oxygen in the neighbourhood of the boiling point.

Date	Time		Pressure in m.m. mercury	Mean of a series	Deviation from the mean
6 Febr. '08	$4^h\,31'$	large pattern (little)	806.34	806.71	—0.37
excess of pressure	4 46	small „ (much)	806.55		—0.16
Series I	5 0	„ „ (little)	806 98		+0.27
	5 8	large „ (much)	806.97		+0.26
7 Febr. '08	10 13	small „ (little)	759.47	759.61	—0.14
pressure a little below 760 mm.	10 21	„ „ „	759.75		+0.14
Series II	10 50	„ „ (much)	759.46		—0.15
			759.54		—0.07
	11 12	large „ „	759.35		—0.26
			759 51		—0.10
	11 47	„ „ „	759 76		+0.15
	12 26	small „ (little)	759.84		+0.23
	12 37	large „ (much)	759.82		+0.21
7 Febr. '08	1 20	small „ (little)	806.17	806.26	—0.09
excess of pressure	1 25	large „ (much)	806.30		+0.04
Series III	1 35	small „ (little)	806 31		+0.05

§ 5 *Accuracy of the adjustments.*

From the results of table III we derive the following data.

The deviations from the mean which must be ascribed partly to the regulation of the temperature are small and when reduced to differences of temperature they remain below 0°.005.

The mean of the results of the large and the small pattern derived separately for each series gives:

Series I, large pattern $p =$ 806.65 (2 observations)
small „ 806.76 (2 „)
Series II, large „ $p =$ 759.64 (5 „)
small „ 759.58 (4 „)
Series III, large „ $p =$ 806.30 (1 observation)
small „ 806.24 (2 observations)

The difference between the two means is at the utmost 0.1 mm. which corresponds to $\frac{1^\circ}{800}$. Thence we may conclude that a vapour pressure apparatus is extremely suited for the standardizing of temperatures. The data obtained here show that in this respect the apparatus surpasses the gas thermometer and probably also the resistance thermometer. For the hydrogen thermometer, namely, the error of 2 adjustments amounts to 0 .01 à 0°.02 (comp. § 3 and Comm. N°. 95^e § 8 and N°. 101^a § 3), for the resistance thermometer to 0°.01 (comp. § 3 and Comm. N°. 101^a § 4)[1].

§ 6. *The determination of the boiling point of oxygen.*

With the resistances of Pt'_I given in § 4 we can by means of the data of table II derive the corresponding temperatures on the scale of our hydrogen thermometer B_{III}. To this end we start from the mean of the two data of March 25 and Dec. 18, '07, because these are probably more accurate than those obtained with the thermometer T'_4. To 34.433 and 34.098 Ω correspond the temperatures — 182°.460 and — 183°.040 respectively. To the first belongs the vapour pressure 806.40 m.m. (the mean from the series I and III) to the second 759.61 mm. (series II). Thence follows by means of rectilinear interpolation for 760 mm. at Leiden for the temperature on the thermometer $B_{III} : t = - 183°.035$ and for the normal boiling point (760 mm. on sea-level and 45° northern latitude):

$$t = -183°.030 - 0°.007 = -183°.037$$

on the normal hydrogen thermometer and (comp. table XXV of Comm. N°. 101^b Dec. 1907)

$$\theta = -183°.042 + 0°.056 = -182°.986$$

on the absolute scale.

If we take into consideration the degree of accuracy of the correction to the absolute scale (comp. Comm. N°. 97^b March '07) and the results for the control determinations for the measurement of temperature made as well with the same hydrogen thermometer as with different ones, then it follows that this value does not probably deviate from the real value by more than 0°.03.

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[1] The data of table III also enable us to judge of the accuracy of the adjustment of the resistance. Let the error in the reading of vapour pressure apparatus = 0, which approximately is permissible according to what precedes, then the difference of the means for the series I and III must be ascribed to the error of the measurement of the resistance. This then would be 0°.005.

§ 7. *Vapour pressure determination at lower temperatures.*

For these measurements (comp. § 2 table II) the temperature was directly read on the hydrogen thermometer B_{III}; Pt'_{I} was used for the regulation. The temperatures are — 186°.599 and — 189°.500 (comp. table II). At the same time we obtained a new calibration for Pt_{I}. The determinations were made with only the small vapour pressure apparatus. The results are combined in table IV in the same way as in table III.

In the determinations marked (*a*) about half of the gas was condensed, in those marked (*b*) about $\frac{4}{5}$ of the gas. As was the case for the boiling point no systematic difference resulting from this seems to be perceptible. If we reduce the temperatures to the absolute scale and the pressures to sea-level and 45° northern latitude we find for:

$$\theta = -186°.542 \qquad p = 516.19 \text{ mm.}$$
$$\theta = -189°.442 \qquad p = 366.24 \text{ mm.}$$

TABLE IV. Vapour pressure of oxygen below the boiling point.

Date	Time	Pressure in mm.	Mean of a series	Deviation from the mean
17 Febr. '08 *(a)*	2ʰ 55′	366.06	365.99	+0.07
(a)	3 30	365.90		—0.09
(b)	4 5	366.00		+0.01
(b)	4 25	365.98		—0.01
18 Febr. '08 *(a)*	10 42	515.82	515.83	—0.01
(a)	11 6	515.89		+0.06
(b)	11 30	515.69		—0.14
(b)	11 40	515.94		+0.11

§ 8. *The results compared with those of other observers.*

Of previous determinations those by TRAVERS, SENTER and JAQUEROD[1]) deserve most confidence, especially because these observers used pure oxygen in a closed reservoir. This is not the case with

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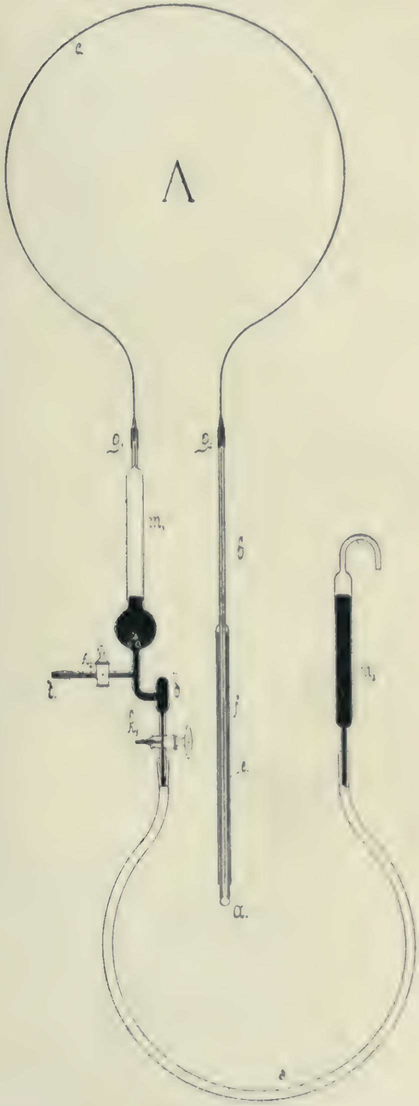
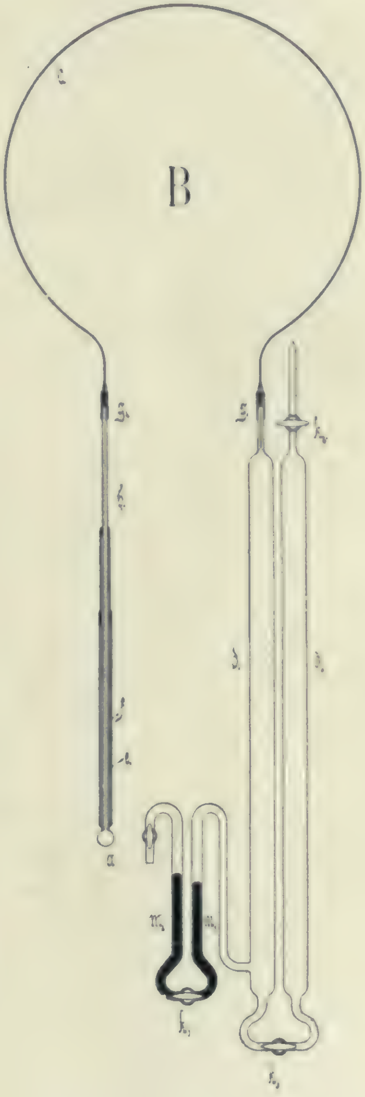
[1]) Phil. Trans. Roy. Soc. Series A. Vol. 200. 1902

(Belongs to Proceedings of the meeting
of Saturday October 31, 1908).

H. KAMERLINGH ONNES and C. BRAAK. "On the measurement of very low temperatures XXI. On the standardizing of temperatures by means of boiling points of pure substances. The determination of the vapour pressure of oxygen at three temperatures."





the other observations where the temperature of a bath of oxygen boiling under atmospheric pressure was determined. For then impurities, nitrogen as well as less volatile substances are unavoidable. It seems that the influence of the latter is paramount; all these results for the boiling point are too high by 0°.3 or more. The first mentioned determinations yield for the boiling point of oxygen — 182°.93 on the normal hydrogen scale. For the pressure 760 mm. is given without indication of a further reduction. Our value for 760 mm. mercury (at 0°) is on the normal hydrogen scale — 183°.030, differing by 0°.10 from the value mentioned above. One of the last determinations is that of Grunmach[1]). He finds — 182°.23. With the correction derived by Hoffmann and Rothe[2]) for the pentane thermometer (— 0°.42) this becomes — 182°.66, a result which after being corrected is still much too high.

If we compare the two observations at lower pressure with those of Travers, Senter and Jaquerod then it appears that both our temperatures are lower by 0°.13. Hence it is clear that a systematic difference exists between the two series.

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[1]) Berliner Sitz. Ber. 1906.

[2]) Zeitschr. f. Instrkd. 27. 1807.

(November 26, 1908).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING
of Saturday November 28, 1908.

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Physics. — "*On the measurement of very low temperatures.* XXII. *The thermo-element gold-silver at liquid hydrogen temperatures.*"

By H. Kamerlingh Onnes and J. Clay. (Communication N°. 107^b from the physical laboratory at Leiden).

(Communicated in the meeting of May 30, 1908).

The thermo-element gold-silver of which, when one of the limbs is kept at 0°, the electromotive force at ordinary temperature is about zero, shows at lower temperatures a more and more rapid increase of electromotive force [1]).

A calibration with the hydrogen thermometer has shown that at the temperatures which can be reached with liquid and solid hydrogen the increase of the electromotive force of this thermo-element per degree becomes large enough to render it suitable for temperature determinations in the area under consideration, while at the temperatures far below the melting point of hydrogen (for the determination of which the helium thermometer must be used for the calibration instead of the hydrogen thermometer) the sensibility of the instrument will be greater still.

The following table may serve to make this clear.

TABLE I. Calibration of the thermo-element gold-silver at hydrogen temperatures.

Temperature read on the hydrogen thermom.	Electromotive force in millivolts.	
	gold-silver	(constantin-steel)
(−216°.01)	(0.11972)	
(−217.416)		(6.8310)
−252.86	0.24742	
−252.93		(7.1315)
−255.34	0.26304	
−258.61	0.28912	
−259.24		(7.1585)

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[1]) Comp. the measurements of J. Clay in his thesis for the doctorate and in Comm. no. 107d from the Physical Laboratory at Leiden.

The third column contains the determinations about the element constantin-steel of Table VI in Comm. N°. 95^a (Sept. '06). Owing to the great lessening of the increase of the electromotive force per degree this element is unfit for the accurate measurement of the lowest temperatures [1]).

We shall soon publish a calibration of the thermo-element gold-silver with the helium thermometer at low temperatures.

Physics. — "*On the change of the resistance of pure metals at very low temperatures and the influence exerted on it by small amounts of admixtures.* II. By H. Kamerlingh Onnes and J. Clay. Communication N°. 107^c from the physical laboratory at Leiden.

(Communicated in the meeting of May 30, 1908).

§ 7. *Supplementary notes to Comm. N°. 99^c* (Sept. '07). We add to it with regard to [2]):

Gold. A formula of the form D has been derived for Au_{V}. The drawing thinner of gold wire has the same influence as we remarked in the comparison of the thin wire Pt_d with Pt_I in Comm. N°. 99^b (Sept. '07) which influence was ascribed to impurities. With two gold wires it was possible by means of analysis to show the difference in composition called forth by drawing.

Mercury. The values given in Comm. N°. 99^c are represented (except at 0°) by the quadratic formula.

$$W_t = 22\,.\,3605\,(1 + 0.00358\,t - 0.06588\,t^2)$$

which for $-197°.87$ gives $O - C = +0.0106$ so that we are led to think that the temperature has not been observed quite accurately enough. Of the metals investigated it seems that mercury is best suited for the measurement of temperatures below the meltingpoint of hydrogen.

Lead. For lead two formulae were derived of the form A' and B' (A and B each time with omission of the term $c\left(\frac{t}{100}\right)^3$), according to which we must reject the observation at — 255°.07 yielding 0.02314 where A' gives 0.01974 and B' 0.01984.

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[1]) Also the element german silver-platinum investigated by Dewar (Proc. Roy. Soc. ser. A, vol. 76 p. 316 sqq. 1905) is unfit for this purpose because of the same fault.

[2]) Observations, formulae and other details are given in J. Clay's thesis for the doctorate, and in Comm. N°. 107*c* for the sections 7 and 8, in Comm. N°. 107*d* for § 9.

§ 8. *Carbon and constantin.* Besides the variations of the metals investigated we have [1]) also investigated to — 262° the variations of resistance of carbon and constantin.

§ 9. *Alloys of Au and Ag.* One of us (J. CLAY) has extended the investigation treated of in the preceding sections to different alloys of gold and silver and has added the determination of the electromotive force of the thermo-element gold-silver. This investigation showed that the theories of RAYLEIGH and LIEBENOW about the thermoelectric origin of the difference in resistance introduced in § 1 (the additive resistance of MATTHIESEN [2])), must be rejected. For the value p, introduced in § 1, the observations mentioned yield with a gold wire of 1 m. in length and 1 mm.² in section per volume procent silver added

$$p = 0.00360 \ \Omega .$$

Mathematics. — "*On certain twisted sextics*". By Mr. M. STUYVAERT at Ghent. (Communicated by Prof. JAN DE VRIES).

(Communicated in the meeting of October 31, 1908).

Prof. JAN DE VRIES has had the goodness to send us an interesting paper which he has published in the Proceedings of the Koninklijke Akademie van Wetenschappen at Amsterdam, entitled "*On twisted curves of genus two*" (26 May 1908).

The greater part of this paper is concerned with twisted curves of genus two and of order five or six. We shall here offer a rapid survey of the results to be obtained when we apply to these curves the elementary properties of matrices, a subject upon which we have recently published a volume: *Cinq Etudes de Géométrie analytique* (Ghent, VAN GOETHEM, 1908). We shall here occupy ourselves only with curves of order six and we shall content ourselves with observing that the quintic can be treated by analogous but more simple proceedings.

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[1]) Cf. footnote 1 to § 7.

[2]) With regard to the deviation from MATTHIESEN's theorem at liquid hydrogen temperatures, mentioned sub § 1, we also refer to the publications mentioned in the footnote 1 to § 7.

We have to return first to a circular sextic of which we have sketched the theory in the Comptes-rendus de l'Académie des Sciences of Paris (27 July 1908, pages 322—324); we shall remember briefly, whilst completing them, the immediate properties and we shall then point out how we deduce from it the theory of the most general sextic of genus two.

Let me say, by the way, that the method we make use of has a more general scope. Indeed, we see the theoretical possibility of using it for every algebraic twisted curve. For HALPHEN defines such a curve as the locus of a point the coordinates of which are algebraic functions of a same parameter t; each of these coordinates is thus connected with t by an integer algebraic equation; it suffices to put down the conditions in order that these three equations be satisfied by a same value of t; and it is in several ways possible to express these conditions by the disappearance of a matrix: the representation of CAYLEY by means of cone and monoid forms at bottom a solution of the problem. We have pointed out an other one in our *Cinq Etudes* (p. 60) and others can still be found; but most of the times the curve under consideration is found accompanied by curves of an inferior order.

1. Let us now return to the real subject of our paper.
Let

$$S_i \equiv a_i\,(x^2 + y^2 + z^2) + s_i \quad (i = 1, 2, 3, 4, 5, 6)$$

be in rectangular cartesian coordinates the equations of six independent spheres (the functions s_i are linear in x, y, z). The equations

$$\frac{S_1}{S_4} = \frac{S_2}{S_5} = \frac{S_3}{S_6} \quad \text{or} \quad \left\|\begin{matrix} S_1 & S_2 & S_3 \\ S_4 & S_5 & S_6 \end{matrix}\right\| = 0 \quad . \quad . \quad . \quad . \quad (1)$$

represent besides the imaginary circle at infinity a twisted curve γ_6 of order six, of genus two, containing six points of the imaginary circle at infinity.

We shall now and then write the equations (1) in abridged form $\|S_1\ S_4\| = 0$ and we shall suppose emphatically that the matrix $\|a_1\ a_4\|$ is not zero, without which $x^2 + y^2 + z^2$ might cause by subtraction the denominators of the fractions (1) to disappear and the curve would be of order five of which the theory is analogous to that of γ_6, but simpler.

The curve γ_6 is on ∞^2 cyclids $|\alpha_1\ S_1\ S_4| = 0$, two of which intersect each other still according to a quadrisecant circle of γ_6. The equations of such a circle can be written

$$\left.\begin{aligned}\Sigma \lambda_1 S_1 &= \lambda_1 S_1 + \lambda_2 S_2 + \lambda_3 S_3 = 0, \\ \Sigma \lambda_1 S_4 &= \lambda_1 S_4 + \lambda_2 S_5 + \lambda_3 S_6 = 0\end{aligned}\right\} \quad . \; . \; . \; . \quad (2)$$

and we can easily deduce from them a theory pretty well detailed of the congruence of these quadrisecant circles of γ_6. Thus we see that this congruence is of order one and of class three; that those circles which pass through a fixed point of γ_6 generate a cyclid having this point as a node; that those circles of which the plane passes through a fixed point generate a surface of order seven; we find the surface which is generated by those circles resting on a right line or on a curve, etc., etc. The most important result is that the planes of these circles envelop a cubic scroll Sc_3.

Every sphere containing a quadrisecant circle of γ_6 has an equation of the form

$$\Sigma \lambda_1 (S_1 - k S_4) = 0 \quad . \; . \; . \; . \; . \; . \; . \; , \quad (3)$$

and it contains the two points for which we have $S_1 = kS_4$, $S_2 = kS_5$, $S_3 = kS_6$. When k varies these two points describe the fundamental involution discussed by Prof. JAN DE VRIES; we simply shall call *couples*, the couples of points of this involution. The chords of *couples* are the rectilinear generatrices of the surface Sc_3.

Among the surfaces $a_1 S_1 S_4$ circumscribed about γ_6, we must distinguish the two following

$$|a_1 S_1 S_4| = 0, \qquad |a_4 S_1 S_4| = 0 \quad . \; . \; . \; . \; . \; . \quad (4)$$

They are *circular cubics* and they determine a pencil the base of which completes itself by means of the circle at infinity and of the line

$$\| a_1 \, . \, a_4 \quad S_1 \quad S_4 \| = 0 \; ; \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

by subtraction of the columns this matrix is reduced to $\| a_1\, a_4\, s_1\, s_4$ and represents a right line q, quadrisecant of γ_6, double line of the surface Sc_3 and meeting all the chords of the *couples*.

2. Let us write the equations of the sphere S_i in the more complete form

$$S_i = a_i(x^2 + y^2 + z^2) + b_i x + c_i y + d_i z + f_i = 0,$$

let us put the matrix

$$M = \| a_i \; b_i \; c_i \; d_i \; f_i \| \quad (i = 1, 2, 3, 4, 5, 6)$$

and let us call M_i the determinant deduced from this matrix by the omission of the row of rank i and affected by the sign $+$ or $-$ according to i being even or odd; we shall then have evidently

$$\left.\begin{aligned}\Sigma M_i a_i = \Sigma M_i b_i = \Sigma M_i c_i = \Sigma M_i d_i = \Sigma M_i f_i = 0, \\ \Sigma M_i S_i \equiv 0. \qquad (i = 1, 2, 3, 4, 5, 6)\end{aligned}\right\} \quad . \; . \quad (6)$$

Consequently the two following equations are perfectly equivalent

$$\left.\begin{array}{l}(S_1-kS_4)(M_4+lM_1)+(S_2-kS_5)(M_5+lM_2)+(S_3-kS_6)(M_6+lM_3)=0\\(S_1-lS_4)(M_4+kM_1)+(S_2-lS_5)(M_5+kM_2)+(S_3-lS_6)(M_6+kM_3)=0.\end{array}\right\}. \quad (7)$$

They represent visibly one as well as the other the sphere brought through the two *couples* defined by the parameters k and l. Each of these equations can, by putting ΣM_4S_1 instead of $M_4S_1+M_5S_2+M_6S_3$, etc., be written in the abridged form

$$\Sigma M_4S_1+(k+l)\Sigma M_1S_1-kl\Sigma M_1S_4=0. \quad . \quad . \quad . \quad (8)$$

For k and l variable we have a double infinity of spheres or rather a net of spheres, for they all pass through two fixed points D_1 and D_2 of γ_6, points for which the three following expressions are annulled at the same time:

$$\Sigma M_4S_1, \qquad \Sigma M_1S_1 \text{ or } -\Sigma M_4S_4, \qquad \Sigma M_1S_4.$$

These points D_1 and D_2 are on any sphere containing two *couples*, thus also in the plane of two *couples* of which the chords cut each other (on the quadrisecant q); so $D_1\,D_2$ is the simple line of the surface Sc_3 through which pass all the bitangent planes of this surface.

We find that the line D_1D_2 has as equations

$$\left\|\begin{array}{ccc}\Sigma S_1M_4 & \Sigma S_1M_1 & \Sigma S_4M_1\\ \Sigma a_1M_4 & \Sigma a_1M_1 & \Sigma a_4M_1\end{array}\right\|=0. \quad . \quad . \quad (9)$$

In order that it may mix up with the line q or that the surface Sc_3 may be a special cubic scroll of CAYLEY we must have the condition

$$\Delta=\left|\begin{array}{cc}\Sigma a_1M_1 & \Sigma a_1M_4\\ \Sigma a_4M_1 & \Sigma a_4M_4\end{array}\right|=0. \quad . \quad . \quad . \quad . \quad (10)$$

The determinant Δ is the product out of the columns of the two matrices $a_1\ a_4$ and $M_1\ M_4$; its disappearance corresponds to a special case in which the curve γ_6 acquires certain exceptional, remarkable properties which cannot be mentioned here for want of space.

3. Since the curve γ_6 belongs to the base of a pencil of cubic circular surfaces and to a surface Sc_3 which is not an element of this pencil, it is found on all the cubic surfaces of a certain net. Any two of these surfaces intersect each other according to the curve γ_6, the quadrisecant q, and a conic c_2. This conic cuts γ_6 in six points and reciprocally every conic cutting γ_6 six times belongs to a pencil of circumscribed cubic surfaces.

The preceding allows us to write the equations of γ_6 in a new form. Two circular cubic surfaces containing the curve have equations of the form

$$|a_1 S_1 S_4| \equiv |a_1 s_1 s_4| + (x^2 + y^2 + z^2)\,|a_1 s_1 a_4| = 0,$$
$$|a_4 S_1 S_4| \equiv |a_4 s_1 s_4| + (x^2 + y^2 + z^2)\,|a_4 a_1 s_4| = 0.$$

The intersection of these surfaces from which the circle at infinity will be subtracted will verify the relations

$$\left\| \begin{array}{ccc} x^2 + y^2 + z^2 & |a_1 s_1 s_4| & |a_4 s_1 s_4| \\ 1 & |a_1 a_4 s_1| & |a_1 a_4 s_4| \end{array} \right\| = 0\,, \quad . \quad . \quad . \quad (11)$$

which thus represent the curve γ_6 with its quadrisecant q: the determinant of the two last columns is annulled for the scroll S_3.

We thus find that the curve γ_6 accompanied by its quadrisecant q constitutes a special case of a curve of order seven and genus **5**, annulling a matrix of three columns and two rows, one of quadratic forms, the other of linear forms, curve of order seven which we have discussed in our *Cinq Études* (p. **44**) in giving the bibliography.

By causing the matrix (11) to be preceded by a line of constants we find the net of cubic surfaces circumscribed to γ_6. Two of these surfaces intersect each other still according to a sexisecant conic of γ_6, conic of which the equations are

$$\left.\begin{array}{l} \mu_1 (x^2 + y^2 + z^2) + \mu_2\,|a_1 s_1 s_4| + \mu_3\,|a_4 s_1 s_4| = 0\,, \\ \mu_1 \qquad\qquad\qquad + \mu_2\,|a_1 a_4 s_1| + \mu_3\,|a_1 a_4 s_4| = 0. \end{array}\right\} \quad . \quad . \quad (12)$$

The second of these equations represents the plane of the conic; we see that this plane is parallel to the line q and that every plane parallel to q contains a sexisecant conic of γ_6.

The equations (12) represent the congruence of the sexisecant conics of γ_6; it is a *particular* case of a congruence considered by Mr. MONTESANO (*Atti Accad. Torino*, 1892); we see that it is of order one and of class one; that the planes of those conics which break up into two trisecant lines of γ_6 envelop a cylinder of class four etc.

If we let the matrix (11) be followed by a column of which the first element is an arbitrary linear form α_x and the second an arbitrary constant β, we obtain a matrix which is annulled for eight points of which six are on γ_6 and two are on the quadrisecant; they are the intersections of γ_6 and of q with the sphere

$$(x^2 + y^2 + z^2)\,\beta - \alpha_x = 0.$$

If we make in this equation β and the coefficients of α_x to vary, we have all the possible spheres; on the other hand we verify immediately that the eight points in question and any sexisecant conic of γ_6 are always on a same quadric.

In other words: every sexisecant conic of γ_6 plays a part analogous to that of the imaginary circle at infinity which is also a sexisecant conic of γ_6.

4. This last observation suggests an other one of greater importance. By means of a linear transformation which replaces the circle at infinity by an other conic the curve γ_6 becomes the most general twisted sextic of genus two. Really Halphen (*École polytechnique* 52^{ème} cah., 1882) has shown that such a sextic is the partial intersection of two cubic surfaces which have still a line and a conic in common and it is implied that this right line and this conic do not meet. So let us take the plane of the conic as face x_1 of the tetrahedron of reference and the right line as edge x_2x_3 of this tetrahedron. The equation of one of the cubic surfaces has the form

$$x_1 a_x^2 = b_x^2 c_x, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

the second member being independent of x_1; $b_x^2 = 0$ is the cone with vertex $x_2x_3x_4$ perspective to the conic of the plane x_1; the line x_2x_3 belonging to the surface must annul the linear form c_x and consequently also the quadratic form a_x^2.

For the same reasons an other cubic surface circumscribed to the considered system of lines has as equation

$$x_1 a_x'^2 = b_x^2 c'_x, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where $a_x'^2$ and c'_x pass still through the line x_2x_3.

Omitting the conic $x_1 = 0, b_x^2 = 0$, the intersection of these two surfaces annuls the matrix

$$\left\| \begin{matrix} x_1 & c_x & c'_x \\ b_x^2 & a_x^2 & a_x'^2 \end{matrix} \right\| \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Thus every sextic of genus two forms with its quadrisecant a degenerated system of a curve of order seven and of genus five; this system annuls a matrix of three columns and two rows, one of linear forms, the other of quadratic forms where the elements of two columns are annulled for a same line.

Now it is easy to see that any such matrix leads back to an other of six quadrics having one conic in common. And really, the quadrics a_x^2 and $a_x'^2$ passing through the line $c_x c'_x$ can be replaced by $c_x p_x + c'_x q_x$ and $c_x p'_x + c'_x q'_x$; then two determinants deduced from the matrix (15) can be written:

$$x_1(c_x p_x + c'_x q_x) - c_x b_x^2 = 0, \quad x_1(c_x p'_x + c'_x q'_x) - c'_x b_x^2 = 0,$$

whence for the points which do not annul c_x and c'_x at the same time,

$$\left\| \begin{matrix} c_x & x_1 q_x & b_x^2 - x_1 q'_x \\ c'_x & b_x^2 - x_1 p_x & x_1 p'_x \end{matrix} \right\| = 0 ;$$

by multiplying the terms of the first column by x_1 and by applying in any arbitrary way the addition of the rows and the columns, there is always a matrix of six quadratic forms annulling itself for the conic $x_1 = b_x^2 = 0$.

The projective theorems relating to the circular sextic γ_6 can thus be translated into properties of the most general sextic of genus two. It is superfluous to write down how these theorems run; we shall quote but one as an example: in every sextic of genus two the planes of the sexisecant conics pass through a fixed point of the quadrisecant.

5. If the intersection of the two cubic surfaces considered in the preceding (13) and (14) is completed by a line and a conic having a point in common, we have not a special case of the preceding case, in the sense of HALPHEN; but this line and this conic form a special case of a twisted cubic and the sextic is then of order three. Really in this case the equations (13) and (14) can be such that the line $x_2\, x_3$ annuls a_x^2, a'^2_x and b_x^2 without annulling c_x of c'_x and the matrix

$$\left\| \begin{matrix} x_1 & c_x & c'_x \\ b_x^2 & a_x^2 & a'^2_x \end{matrix} \right\|$$

has then the elements of its second row disappearing for a same line.

By this proceeding we can study the sextic of genus three; we can refind the univalent correspondence between its points and its trisecants, correspondence found by Mr. F. SCHUR (*Math. Ann.* vol. 18); we can bring back the representation of the curve to a matrix of twelve linear forms which we have studied in our *Cinq Etudes* and in the *Bulletins de l'Académie royale de Belgique* (May 1907), etc.

Ghent, Oct. 26, 1908.

Mathematics. — "*On the combinatory problem of* STEINER." By Dr. J. A. BARRAU. Communicated by Prof. D. J. KORTEWEG.

(Communicated in the meeting of October 31, 1908).

In its most general form this problem runs as follows:

for which values of n and in how many really different[1]) *ways is it possible to write down a number of combinations p to p of n elements in such a way that all combinations q to q appear in it, each one time?*

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[1]) i. e. which do not pass into each other by means of substitutions of the n elements.

A geometrical way of putting the question is this:
which combinatory configurations whose points S_0 are represented by the combinations q to q of n letters, whilst the combinations p to p represent its Sp_{p-q}, possess systems of Sp_{r-q} containing all points of the Cf each one time and how many types of such systems appear in each definite case?

The first question gave rise to investigations for $= 3$, $q = 2$, the *triple systems* (KIRKMAN, REISS, NETTO, MOORE, HEFFTER, BRUNEL [1])); the second question is discussed by J. DE VRIES [2]) and CARP [3]).

Here some results are communicated for $p > 3$, $q > 2$. We adhere for this to the first form of the question and we call a system as is demanded there an $S(p, q), n$.

If we isolate in an $S(p, q), n$ all sets of p having in common a certain arbitrarily chosen letter, and if we omit that letter from it, an $S(p—1, q—1), n—1$ is generated; repetition of the operation gives rise to an $S(p—2, q—2), n—2$ and so on; the possibility of an $S(p, q)$ presupposes thus that of a series of systems of lower rank [4]), which series can be broken off at

$$S(p-q+2, 2),\ n-q+2$$

Inversely all imaginable systems are acquired by completion of systems commencing with $q = 2$.

So we can expect:

out of $S(3, 2)$, $n = 7$: $S(4, 3)$, $n = 8$ . . . . *A*
out of $S(3, 2)$, $n = 9$: $S(4, 3)$, $n = 10$ . . . . *B*
$S(5, 4)$, $n = 11$ . . . . *C*
$S(6, 5)$, $n = 12$ . . . . *D*

etc. We will show that the four systems mentioned exist *each of them in one type.*

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[1]) *Cambridge and Dublin Math. Journal* II, 1847; *Journal f. d. r. u. a. Mathem.* 56, 1859; *Mathem. Annalen* 42, 1893; 43, 1893; 49, 1897; 50, 1898; *Association française, Congrès de Bordeaux* 1895; *Journal de Liouville* (5) VII, 1901.

[2]) *Versl. en Meded. Kon. Akad. v. Wet.* 3rd series, VI, p. 13, 1889; *Mathem. Annalen* 34, 35, 1889, '90.

[3]) Dissertation, Utrecht 1902, p. 38.

[4]) For *each* system of the series the condition must be satisfied: $\binom{n}{q}$ divisible by $\binom{p}{q}$. Thus there will be no $S(6, 4), n = 15$, although $\binom{15}{4}$ is divisible by $\binom{6}{4}$, on account of the impossibility of an $S(5, 3)$ $n = 14$: $\binom{14}{3}$ is not divisible by $\binom{5}{3}$.

A. An $S(4,3)$, $n=8$ consists of $\binom{8}{3}:\binom{4}{3}=14$ quadruplets, so it is a schematic Cf. $(8_7, 14_4)$. If we add to the triplets of an $S(3,2)$, $n=7$, that is of a Cf. (7_3) a new letter, and if out of the quadruplets thus formed we choose one, then in the completion with seven new quadruplets sought for the pairs of the selected triplets must appear still twice; so a new quadruplet remains, complementary to the one selected.

This holds for each quadruplet; the whole completion is thus complementary and only possible in one way [1]).

B. If in an $S(4,3)$, $n=10$, that is a Cf. $(10_{12}, 30_4)$, we choose an arbitrary quadruplet 1 2 3 4, each pair of these letters appears in three more quadruplets; so there are 18 more such quadruplets. Then each single letter appears two times more, completed with triplets out of 5, 6, 7, 8, 9, 0, which triplets form thus together a Cf. $(6_4, 8_3)$. Of the whole system only three quadruplets out of 5, 6, 7, 8, 9, 0 remain, which in pairs may have at most only two letters in common. Such systems of three exist however only in one type [2]), as:

5 6 7 8 ; 5 6 9 0 ; 7 8 9 0,

with which the system to be formed must commence. The eight triplets of letters missing here form of necessity the Cf. $(6_4, 8_3)$, which breaks up only in *one* way into four pairs completing each other. If we complete these pairs respectively with 1, 2, 3 and 4 (in which order is irrelevant) the following quadraplets are formed:

1 5 7 9 ; 2 5 7 0 ; 3 5 8 9 ; 4 5 8 0
1 6 8 0 ; 2 6 8 9 ; 3 6 7 0 ; 4 6 7 9.

The entire further completion is now determined and *must* run as follows:

1 4 5 6 ; 1 2 5 8 ; 2 3 7 9 ;
2 3 5 6 ; 1 2 6 7 ; 2 3 8 0 ;
1 3 7 8 ; 1 3 5 0 ; 2 4 5 9 ;
2 4 7 8 ; 1 3 6 9 ; 2 4 6 0 ;
1 2 9 0 ; 1 4 7 0 ; 3 4 5 7 ;
3 4 9 0 ; 1 4 8 9 ; 3 4 6 8 .

Now that with this the existence of only *one* type is assumed, we can give it a simpler form; we shall do this in two ways.

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[1]) The scheme $(8_7, 14_4)$ indicates in the measure-polytope B_4 the vertices, forming with point zero and its opposite vertex together a cross-polytope C_4 (*Nieuw Archief v. Wisk.* 2nd Series, VII, p. 255).

[2]) The complementary type of a division of six elements into three pairs

We in the first place remember that the $S(3,2)$, $n=9$ deduced from $S(4,3)$, $n=10$ is *regular commutative* (Moore), i. e. that its group possesses a regular commutative subgroup of the type:

$$\begin{array}{ccccccccc}
1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\
2 & 3 & 1 & 5 & 6 & 4 & 8 & 9 & 7 \\
3 & 1 & 2 & 6 & 4 & 5 & 9 & 7 & 8 \\
4 & 5 & 6 & 7 & 8 & 9 & 1 & 2 & 3 \\
5 & 6 & 4 & 8 & 9 & 7 & 2 & 3 & 1 \\
6 & 4 & 5 & 9 & 7 & 8 & 3 & 1 & 2 \\
7 & 8 & 9 & 1 & 2 & 3 & 4 & 5 & 6 \\
8 & 9 & 7 & 2 & 3 & 1 & 5 & 6 & 4 \\
9 & 7 & 8 & 3 & 1 & 2 & 6 & 4 & 5
\end{array}$$

Indeed, an $S(3,2)$, $n=9$ appears if we submit the triplets

1 2 3 ; 1 4 7 ; 1 5 9 ; 1 6 8

to all the substitutions of this group.

If we now add to each of these twelve triplets a zero and if we submit the quadruplets

1 2 4 5 and 1 2 6 9

to the substitutions of the group, then the $12+18=30$ quadruplets of the $S(4,3)$, $n=10$ are formed.

Secondly we observe, that the system is cyclic and appears among others by submitting the quadruplets

1 2 3 7 ; 1 2 4 5 ; 1 3 5 8

to the cycle (1 2 3 4 5 6 7 8 9 0).

C. If we choose out of an $S(5,4)$, $n=11$, that is a Cf. $(11_{30}, 66_5)$, a quintuple 1 2 3 4 5, then all triplets of it must appear still three times, all pairs moreover still two times, the single letters afterwards three times, with which the $10\times 3+10\times 2+5\times 3=65$ remaining quintuplets of the system are exhausted. The single letters are completed with quadruplets out of 6, 7, 8, 9, 0, a, which may have at most three letters in common and which form together a Cf. $(6_{10}, 15_4)$, consisting of five $(6_2, 3_4)$ as appeared in *B*. Of this but *one* type exists [1]), so that e. g. the $S(5,4)$ commences with:

1 8 9 0 a	2 7 9 0 a	3 7 8 0 a	4 7 8 9 a	5 7 8 9 0
1 6 7 0 a	2 6 8 9 a	3 6 8 9 0	4 6 8 0 a	5 6 9 0 a
1 6 7 8 9	2 6 7 8 0	3 6 7 9 a	4 6 7 9 0	5 6 7 8 a

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[1]) Deduced from the well-known system of five three-divisions of six elements of Serret.

The further constitution is now determined and must run as follows:

1 2 6 9 0	1 4 6 9 *a*	2 3 6 0 *a*	2 5 6 7 9	3 5 6 7 0
1 2 7 8 *a*	1 4 7 8 0	2 3 7 8 9	2 5 8 0 *a*	3 5 8 9 *a*
1 3 6 8 *a*	1 5 6 8 0	2 4 6 7 *a*	3 4 6 7 8	4 5 6 8 9
1 3 7 9 0	1 5 7 9 *a*	2 4 8 9 0	3 4 9 0 *a*	4 5 7 0 *a*

1 2 3 6 7	1 2 5 6 *a*	1 3 5 6 9	2 3 4 6 9	2 4 5 6 0
1 2 3 8 0	1 2 5 7 0	1 3 5 7 8	2 3 4 7 0	2 4 5 7 8
1 2 3 9 *a*	1 2 5 8 9	1 3 5 0 *a*	2 3 4 8 *a*	2 4 5 9 *a*
1 2 4 6 8	1 3 4 6 0	1 4 5 6 7	2 3 5 6 8	3 4 5 6 *a*
1 2 4 7 9	1 3 4 7 *a*	1 4 5 8 *a*	2 3 5 7 *a*	3 4 5 7 9
1 2 4 0 *a*	1 3 4 8 9	1 4 5 9 0	2 3 5 9 0	3 4 5 8 0

A simple form of the system[1]) is obtained by submitting the quintuplets

1 2 3 4 0; 1 2 3 5 8; 1 2 3 6 7;
1 2 4 5 9; 1 2 4 6 8; 1 2 5 7 0

to the cycle:

(1 2 3 4 5 6 7 8 9 0 *a*).

D. By a reasoning analogous to that in section *A* is evident that $S(6,5)$, $n = 12$, that is a Cf. $(12_{66}, 132_6)$ *must* appear by complementary completion of $S(5,4)$, $n = 11$, so it appears only in *one* type.

In general out of each

$$S(p = q + 1, q),\ n = 2q + 3$$

is formed by complementary completion an

$$S(p = q + 2, q + 1), n = 2q + 4.$$

Passing to systems $S(p, q = 2), n$ for arbitrary p[2]), we observe that for their existence is necessary at least:

$$\frac{n(n-1)}{1.2} \text{ divisible by } \frac{p(p-1)}{1.2},$$

and

$$n-1 \quad \text{divisible by} \quad p-1,$$

which conditions are fulfilled only by the two series of numbers

$$\begin{array}{ll} I & n = p\,(p-1)\,.\,x + 1 \\ II & n = p\,(p-1)\,.\,x + p \end{array} \Bigg\} \; x = 0, 1, 2, \ldots\ldots$$

---

[1] A $S(5,4)$, $n = 11$ was given by Lea (*Educ. Times* IX), the method in which this was generated is unknown to me, as this publication was not attainable for me; however, the system must be of the same type. We remark moreover, that to prove this, it is not sufficient to assert that all remainders have a fixed type, comp. Martinetti (*Annali di Matem.* (2) XV). The same holds for *A*, *B* and *D*.

[2] These $S(p,2)$ are to be distinguished from the systems of Brunel, in which each set of p is regarded as containing only the p pairs of elements succeeding each other (*Proc. Verb. Soc. de Bordeaux*, 1895/96, p. 58 and 1898/99, p. 59, 71).

The term $x = 0$ has no significance in I; in II it indicates that when writing all $n = p$ letters we have written at the same time all pairs of those letters. This system $II, x = 0$ will be of service in what follows.

We shall now give a more extensive form to the *multiplication-theorem* of **Netto** (l.c. § 3) which becomes:

Out of an $S(p,2)\, n_1$ and an $S(p,2), n_2$ an $S(p,2)\, n_1 n_2$ can be deduced, if one disposes of a system of $p(p-1)$ permutations of p elements, in which a couple of elements never occupies the same place.

For, if the elements of the two systems are resp. $a_k\ (k = 1,2 \ldots . n_1)$ and $b_l\,(l = 1,2, \ldots . . n_2)$ we can then designate $n_1 n_2$ new elements by $c_{k,l}$. Of these elements we form *three* kinds of p sets of p, namely:

1st. out of *each* set of p $a_1\, a_2 \ldots . a_p$ new p-sets:

$$c_{1,l}, c_{2,l}, \ldots , . c_{p,l}\ (l = 1,2 \ldots \ldots n_2);$$

2nd. out of *each* set of p $b_1 b_2 \ldots . b_p$ new p-sets:

$$c_{k,1}, c_{k,2}, \ldots \ldots c_{k,p}\ (k = 1,2 \ldots \ldots n_1);$$

3rd. out of *each* set of p $a_1 a_2 \ldots . a_p$, combined with *each* set of p $b_1 b_2 \ldots . b_p$ new p-sets:

$c_{1,l_1}, c_{2.l_2} \ldots \ldots c_{p,l_p}$, where $l_1 \ldots \ldots l_p$ are every time the same as the indices $1 \ldots . p$ of the set of p of b, yet differ $p-1$ times in order of succession according to the $p-1$ permutations of the system of permutations supposed as disposable.

It is clear that in this way a couple of the new elements can never appear more than once whilst the number of formed sets of p amounts to:

$$n_2 \frac{n_1(n_1-1)}{p(p-1)} + n_1 \frac{n_2(n_2-1)}{p(p-1)} + p(p-1) \frac{n_1(n_1-1)}{p(p-1)} \cdot \frac{n_2(n_2-1)}{p(p-1)} = \frac{n_1 n_2(n_1 n_2-1)}{p(p-1)},$$

so that really an $S(p,2), n_1 n_2$ is formed.

Now we dispose of such a permutation-system, when:

1) $p = 4$: the twelve even permutations;

2) p *prime*, the system then consists of:

$$(1,\ 2,\ 3,\ 4 \ldots \ldots . p)_{cyc.}$$
$$(1,\ 3,\ 5,\ 7 \ldots \ldots . p-1)_{cyc.}$$
$$(1,\ 4,\ 7,\ 10 \ldots \ldots .)_{cyc.}$$
$$\ldots \ldots \ldots \ldots \ldots \ldots$$
$$(1,\ p,\ p-1,\ p-2 \ldots 2)_{cyc.}{}^{1})$$

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1) Comp. e.g. **Brunel**, *Proc. Verb. Soc. de Bordeaux* 1894/95, p. 56, or **Ahrens**. *Mathematische Unterhaltungen*, p. 272: "Promenaden von n^2 Personen zu je n". It is not decided whether also other values of p allow a solution.

(For $p = 3$ the system just contains the total group and so the theorem of **Netto** reappears).

So we have:

The possibility of the multiplication is assured for $p = 4$ *or prime.*

Now by taking as factors $n_1 = n_2 = p$, so term $II, x = 0$, we obtain:

For $p = 4$ *or prime the existence of* $S(p,2), n = p^2$ *is assured.*

Such a system, term $II, x = 1$ is, regarded as Cf.-scheme, a Cf. $\{p^2{}_{p+1}, p(p+1)_p\}$: its p-sets can be divided into $(p+1)$ principal groups of p, each of which contains all the p^2 elements.

We can now give in a more extensive from an other theorem of **Netto** (l.c. § 2), which becomes here:

Out of an $S(p, 2), n$ *an* $S(p, 2), (p-1)n + 1$ *can be formed if we have at our disposal a scheme of* $(p-1)^2$ *sets of* p *out of* $p(p-1)$ *elements, having mutually not more than one element in common, which elements must be able to break up into* p *principal groups of* $(p-1)$.

For, we can add to the elements $a_{1,1}, a_{1,2} \ldots . a_{1,n}$ of the given system $(p-2)$ series of new ones:

$$\begin{array}{cccc} a_{2,1} & , a_{2,2} & , \ldots . & a_{2,n} \\ \ldots & \ldots & \ldots & \ldots \\ a_{p-1,1} & , a_{p-1,2} & , \ldots . & a_{p-1,n} , \end{array}$$

and moreover a last element a_0.

For each set of p of the given system we must now form out of the $p(p-1)$ elements with the same second indices a scheme as the one indicated in the theorem, taking care that always the $(p-1)$ elements with equal second index form a principal group. Finally we must add to each principal group the element a_0, by which also these principal groups are completed to p. It is clear that the sets of p formed in this way can have two by two at most but *one* element in common, while their number amounts to:

$$(p-1)^2 \cdot \frac{n(n-1)}{p(p-1)} + n = \frac{\{(p-1)n+1\}\{(p-1)n\}}{p(p-1)},$$

so that an $S(p, 2), (p-1)n + 1$ is formed.

The possibility of the method now depends on the presence of a scheme:

$$\{p(p-1)_{p-1} , (p-1)^2_p\}$$

or, replacing p by $p-1$, of

$$\{p(p+1)_p , p^2_{p+1}\},$$

but that is just the notation of the above-mentioned $S(p, 2), n = p^2$, if but in the diagram we exchange rows and columns. It satisfies, moreover the further conditions; so we have:

The deduction of an $S(p,2)$, $(p-1)n+1$ *out of an* $S(p,2)$, n *is assured, when* $p=5$ *or a prime number* $+1$.

If we apply this to $n=p$, we find:

The existence of $S(p,2)$, $n=p(p-1)+1$ *is assured for* $p=5$ *or a prime number* $+1$.

These systems form the term I, $x=1$; as Cf.-schemes they are Cff. $\{p(p-1)+1_p\}$.

It is clear that their remainders to *one* element again become $S(p-1,2)$, $n=(p-1)^2$, that is term II, $x=1$ out of the series $p-1$.

In cyclic form we find:

$n=13$, $p=4$: (1, 2, . . 5, . . 7) cyc.
$n=21$, $p=5$: (1, 2, . . 5, . . 15, . . 17 . .) cyc.
$n=31$, $p=6$: (1, 2, . . 5, . . 7 . . 14, . . 22 . .) cyc. [1]

We finally pass on to the generation of an $S(4,2,)$ $n=25$.

As Cf. the system is a Cf. $(25_8, 50_4)$, the remainder to each quadruplet is a Cf. (21_4). The latter must have the property that the non-united elements may be united to triplets, so that out of it arises a Cf. $(21_4, 28_3)$ which breaks up into four principal-7-sides [2]). By imagining the seven lines of such a 7-side to be every time convergent to *one* point and the four points of convergence to be collinear, the desired Cf. $(25_8, 50_4)$ is formed.

We obtain a solution by submitting

1, . . 3, . . 9, . . 12;
1, . . 8, . . 15 , (completed by 22);
1, . . 2, . . 6 , (in turns completed by 23, 24 and 25);

to the cycle

(1, 2, 3, . . . 21)

and by finally adding:

22, 23, 24, 25.

In like manner we shall find that in general an

$$S(p,2),\ n=2p(p-1)+1,$$

that is a Cf. $\{2p(p-1)+1_{2p},\ 4p(p-1)+2_p\}$, will consist of a

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[1]) Comp. E. Malo, *(Interm. des Mathém.* XVI, p. 63). The $2p$ cycles given there for each p are mutually identical and so they furnish every time but one type.

[2]) Comp. a former paper in these Proceedings (p. 290). In the mean time I have found that the result given there, in as far as it concerns $n=13$ is obtained in about the same way by Brunel (*Journal de Liouville*, 1901), and already in 1899 by de Pasquale, *Rendic. R. Inst. Lombardo* (2) 32, p. 213.

$$\text{Cf. } \{(2p-1)(p-1)_p\},$$

whose missing pairs of elements can be united to sets of $(p-1)$, so that a

$$\text{Cf. } \{2p(p-1)_p,\ p(2p-1)_{p-1}\}$$

is formed which breaks up into p principal-$(2p-1)$-sides.

As in the series $p=4$, just as for $p=3$, the two extensions of the theorems of NETTO can be applied, we can form, in the first set of hundred, systems $S(4, 2)$ for:

$$n = 13,\ 25,\ 49;\ 4,\ 16,\ 40,\ 52,\ 64,\ 76,\ 100.$$

The still missing values are:

$$n = 37,\ 61,\ 73,\ 85,\ 97;\ 28,\ 88,$$

of which 85 might be acquired by 28.

Physics. — "*Remarks on the Leyden observations of the Zeeman-Effect at low temperatures.*" By W. VOIGT. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the Meeting of October 31, 1908).

The observations of KAMERLINGH ONNES and JEAN BEQUEREL [1]) on the ZEEMAN-Effect at exceedingly low temperatures have led to some surprising results, among which are two, very interesting from the theoretical standpoint. These I will try to throw light upon in the following.

I. It has been found, when the observation was made along the optic axis of an uniaxial crystal (where such a body acts as if isotropic) a longitudinal magnetic field being used, that the components of the ZEEMAN-doublet have different intensities. The component on the side of the shorter wave-length had generally (though not always) the greater intensity.

This result seems to show, that in the crystal one sense of rotation is preferred to the other. Therefore it might be interesting, to consider firstly the effect of a magnetic field on a naturally active crystal. I may at this point remark that, contrary to what should be expected, the effects of the natural activity and of the magnetic field do not superpose each other, but rather singular combined effects appear in the neighbourhood of an absorption band.

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[1]) J. BECQUEREL and KAMERLINGH ONNES. These Proceedings February 29th 1908.

The following notation will be made use of:

A, B, C components of magnetic force.
$X\ Y\ Z$ „ „ electric „
$\mathfrak{A}, \mathfrak{B}, \mathfrak{C}$ „ „ magnetic polarization.
$\mathfrak{X}, \mathfrak{Y}, \mathfrak{Z}$ „ „ electric „
$\mathfrak{x}_h, \mathfrak{y}_h, \mathfrak{z}_h$ „ „ electric partial polarizations.
$a_h, b_h, c_h, \delta_h, \varepsilon_h$ parameters.
P external magnetic force, supposed // Z.
v velocity of light in vacuum.

Then the equations of the theory based on the suppositions I have made for an isotropic active body become:

$$\mathfrak{A}' = v\left(\frac{\partial Y}{\partial z} - \frac{\partial Z}{\partial y}\right), \quad \ldots \ldots \quad (1)$$

$$\mathfrak{X}' = v\left(\frac{\partial C}{\partial y} - \frac{\partial B}{\partial z}\right), \quad \ldots \ldots \quad (2)$$

$$\mathfrak{x}_h + a_h\mathfrak{x}'_h + b_h\mathfrak{x}''_h + c_hP\mathfrak{y}'_h = \varepsilon_h X - \delta_h A', \quad \ldots \ldots \quad (3)$$

$$\mathfrak{X} = X + \Sigma\mathfrak{x}_h, \quad \ldots \ldots \quad (4)$$

$$\mathfrak{A} = A + \Sigma\delta_h\mathfrak{x}'_h/\varepsilon_h, \quad \ldots \ldots \quad (5)$$

By a simple calculation we obtain for the so-called complex refractive index $\mathfrak{n}$ in the direction of the magnetic field the value

$$\mathfrak{n} = \sqrt{(1+E)(1+\Theta)} \pm \Delta, \quad \ldots \ldots \quad (6)$$

where

$$E = \Sigma\frac{\varepsilon_h}{p_h \pm c_hP\nu}, \quad \Theta = \nu^2\Sigma\frac{\delta^2_h}{\varepsilon_h(p_h \pm c_hP\nu)},$$

$$\Delta = \nu\Sigma\frac{\delta_h}{p_h \pm c_hP\nu};$$

ν = frequency,

$$p_h = 1 + i\nu a_h - \nu^2 b_h.$$

The double sign ± corresponds to the two waves of circular vibrations and of opposite sense of rotation propagated parallel to the field.

The complex index of refraction $\mathfrak{n}$ is connected with the real index n and with the absorption index $\varkappa$ by the formula $\mathfrak{n} = n(1 - i\varkappa)$. The constants δ_h and c_h measure the natural and the magnetic activity of the crystal. It is seen that even if these two effects are small in general, in the neighbourhood of an absorptionband, where p_h is of the same order as $c_h P\nu$, they do not superpose at all.

If the natural activity vanishes, then also Θ and Δ vanish, and we have

$$\mathfrak{n}^2 = 1 + E,$$

which contains the theory of the longitudinal ZEEMAN effect.

Among the terms arising from the natural activity that of most interest is $\pm \Delta$, which is generally much larger than Θ. This term which has opposite signs for the $+$ and the $-$ rotating waves, but which reaches its maximum at the same place as E, expresses a dissymmetry of the ZEEMAN doublet somewhat similar to that obtained in the experiments of ONNES and BECQUEREL. In order that this dissymmetry should have an appreciable magnitude it is only necessary that $\nu\mathfrak{d}_h$ is commensurable with ε_h. Experience has shown that at the absorption bands of the crystals under consideration, ε_h is very small and so no difficulty is in the way.

Notwithstanding there is lack of agreement between the above formula and observation in two quite different directions. In the first case the observers did not notice any natural activity in the crystals they used, and from the symmetry of these crystals such was not to be expected, except in the case, that at low temperatures the constitution of the molecules changes. On the other hand the observed behaviour by a reversed magnetic field is not in agreement with the above formula.

Both objections disappear if in the formulae (3) we substitute for the terms $\mathfrak{d}_h A'$, $\mathfrak{d}_h B'$, $\mathfrak{d}_h C''$ on the right hand side the terms O, $\mathfrak{d}_h PA'$, $\mathfrak{d}_h PB'$ and in the formulae (5) for the right hand terms resp. A, $B + P\Sigma\, \mathfrak{d}_h \mathfrak{y}_h'/\varepsilon_h$, $C + P\Sigma\, \mathfrak{d}_h \mathfrak{z}_h'/\varepsilon_h$. Such a series of terms corresponds exactly to the symmetry of the magnetic field and leads to the same formula (6) for $\mathfrak{n}$ as that given above; only we have $P\mathfrak{d}_h$ in place of $\mathfrak{d}_h$. By this step both the above mentioned difficulties are removed; however the substitution leads from the sound basis of experience into the region of hypothesis. Observation shows that $\mathfrak{d}_h$ increases as the temperature diminishes.

II. In some crystals of rhombic symmetry it has appeared that in each of the three chief spectra certain absorption lines correspond to nearly the same wave length. If we observe in the direction of an axis of symmetry each of these lines is seen broken up into a doublet when the magnetic field is excited. In the present special case of equal wave length of the lines the distance of the doublet components is the same in some cases, in other cases differs. If we let the axes X, Y, Z, be parallel to the axes of the crystal and call R the direction of magnetic force, ω the direction of propagation of the ray, σ the direction of vibration, then the following table gives the result of observation:

$$R//X\ ,\ \omega//X \begin{cases}\sigma//Y & \alpha_1\\ \sigma//Z & \alpha_1\end{cases}$$

$$\omega//Y \begin{cases}\sigma//Z & \alpha_1\\ \sigma//X & \alpha'_1\end{cases}$$

$$\omega//Z \begin{cases}\sigma//X & \alpha'_1\\ \sigma//Y & \alpha_1\end{cases}$$

$$R//Y\ ,\ \omega//Y \begin{cases}\sigma//Y & \alpha'_2\\ \sigma//Z & \alpha_2\end{cases}$$

$$\omega//Y \begin{cases}\sigma//Z & \alpha_2\\ \sigma//X & \alpha_2\end{cases}$$

$$\omega//Z \begin{cases}\sigma//X & \alpha_2\\ \sigma//Y & \alpha'_2\end{cases}$$

$$R//Z\ ,\ \omega//X \begin{cases}\sigma//Y & \alpha_3\\ \sigma//Z & \alpha'_3\end{cases}$$

$$\omega//Y \begin{cases}\sigma//Z & \alpha'_3\\ \sigma//X & \alpha_3\end{cases}$$

$$\omega//Z \begin{cases}\sigma//X & \alpha_3\\ \sigma//Y & \alpha_3\end{cases}$$

The theory I have developed[1]) makes the laws of the phenomena under consideration depend on 4 × 3 parameters p_h, p_h, g_h, f_h.

p_h and p_h $(h=1, 2, 3)$ are determined by the quasi elastic and damping forces acting on the electron in the crystal, when no magnetic field is excited. g_h $(h=1, 2, 3)$ measure the direct action of the magnetic field on the electron parallel to the axes X, Y, Z; f_h $(h=1, 2, 3)$ determine certain couplings experienced by the electron parallel to these axes.

If we put

$$\begin{aligned} N_1 &= p_1 \overline{p_1} - f_1^2 \nu^2, & N_{23} &= p_2 p_3 - g_1^2 \nu^2,\\ N_2 &= p_2 \overline{p_2} - f_2^2 \nu^2, & N_{31} &= p_3 p_1 - g_2^2 \nu^2,\\ N_3 &= p_3 \overline{p_3} - f_3^2 \nu^2, & N_{12} &= p_1 p_2 - g_3^2 \nu^2, \end{aligned}$$

where as before ν represents the frequency, generally the magnetic effect on an absorption line in the above mentioned cases is given by the following functions:

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[1]) W. Voigt. Gött. Nachr. 28 Juli 1906; Magnetro- und Electrooptik. Leipzig 1908, p. 235 u. f.

$$
\begin{array}{rl}
R//X\ ,\ \omega//X & \begin{cases} \sigma//Y & p_2/N_{23} \\ \sigma//Z & p_3/N_{23} \end{cases} \\
\omega//Y & \begin{cases} \sigma//Z & p_3/N_{23} \\ \sigma//X & (p_1+\bar{p}_1)/N_1 \end{cases} \\
\omega//Z & \begin{cases} \sigma//X & (p_1+\bar{p}_1)/N_1 \\ \sigma//Y & p_2/N_{23} \end{cases} \\
R//Y\ ,\ \omega//X & \begin{cases} \sigma//Y & (p_2+\bar{p}_2)/N_2 \\ \sigma//Z & p_3/N_{31} \end{cases} \\
\omega//Y & \begin{cases} \sigma//Z & p_3/N_{31} \\ \sigma//X & p_1/N_{31} \end{cases} \\
\omega//Z & \begin{cases} \sigma//X & p_1/N_{31} \\ \sigma//Y & (p_2+\bar{p}_2)/N_2 \end{cases} \\
R//Z\ ,\ \omega//X & \begin{cases} \sigma//Y & p_2/N_{12} \\ \sigma//Z & (p_3+\bar{p}_3)/N_3 \end{cases} \\
\omega//Y & \begin{cases} \sigma//Z & (p_3+\bar{p}_3)/N_3 \\ \sigma//X & p_1/N_{12} \end{cases} \\
\omega//Z & \begin{cases} \sigma//X & p_1/N_{12} \\ \sigma//Y & p_2/N_{12} \end{cases}
\end{array}
$$

Supposing now the absorption lines to have the same *positions* in the three chief spectra, then the *real* parts of p_1, p_2, p_3 and also of $\bar{p}_1, \bar{p}_2, \bar{p}_3$ are equal; supposing the *intensities* of the absorption lines to be equal, then the *imaginary* parts are the same. If on the other hand g_1, g_2, g_3 and f_1, f_2, f_3 retain different values from each other, then also N_1, N_2, N_3 and N_{23}, N_{31}, N_{12} have different values from each other. In this case the system of distances between the doublet components obtained from theory agrees exactly with that observed. If the three absorptions are slightly different from each other, then the theoretical distances show small deviations from the mentioned law, which however will scarcely be within the range of perception.

What is interesting in the observations is that if we assume $g_1 = g_2 = g_3$, and therefore $N_{23} = N_{31} = N_{12}$ then theory is not in agreement with experience.

The parameters g_h give the direct influence of the external magnetic field on the vibrating electron. This influence appears then to be different when the field acts along the X-, the Y-, the Z-axis of the crystal. This result seems to me to verify the view I have deduced from other considerations, that the magnetic field inside the molecule, where an electron is in motion, can be very different from that in outside space. Reasoning in this way it is quite natural to imagine that the field inside a molecule of a *crystal* gains different intensities if an external field of constant intensity acts successively parallel to the axes of the crystal.

It is true that in my former publications I have put $g_1 = g_2 = g_3$, because at that time there was no necessity to introduce more complicated suppositions. But the abovementioned observations show that generally g_1 is different from g_2 and g_3.

If we do not accept this difference between the inner and outer field, then we must fall back on the very complicated assumptions of BECQUEREL and ONNES, that the apparent, probably electromagnetic mass of the electron is different parallel to the three axes of the crystal, and that the quasielastic forces in these directions are proportional to these masses. This would lead to the hypothesis of an immense number of different kinds of electrons, say of ellipsoidal form, which during their vibration remain parallel to themselves. The authors do not set forth how the law of the quasielastic forces would be explained. As opposed to the difficulties of this hypothesis I maintain that the above assumption of differences between the inside and outside magnetic fields is much simpler.

III. I should like to mention a general consideration arising from the preceding. It seems to me that by the irresponsible introduction of electrons which have forms masses and signs different from each other, we should lose what has been up to the present one of the chief advantages which characterise the electrontheory; the simplicity of the fundamental conception, and thus make the whole hypothesis of less value. We would have to be content with this depreciated value of the hypothesis, if we were compelled by undeniable results of experience to do so. But up to the present I cannot recognise any such evidence.

The chief objection of J. BECQUEREL to the hypothesis of inner-molecular magnetic fields lies in the fact that the ZEEMAN-effect is notably independent of temperature. But as we do not know anything definite about the cause of the inner field, it appears to me, that one cannot assert anything about the sensibility to temperature with certainty.

In this place I shall mention a consideration which seems to me to carry some weight against the precipitate assumption especially of *positive* electrons.

We learn from the theory of light that in bodies electrons oscillate about positions of equilibrium. Further the electron-theory permits only of forces of electromagnetic nature: the quasielastic forces which bind the electrons to their equilibrium positions must therefore also be of electromagnetic nature. Thus here the only force to be considered, is electrostatic, we know from the theory of potential that an electrostatic field permits of a point-charge moving about a stable position of rest *only inside of a charge of opposite sign distributed over space.* Thus the assumption of *negative electrons* made up to the present time leads to the conception of *positive* electric charges distributed over a definite space. These two hypotheses contain no contradiction.

The assumption of *positive electrons* (of parallel properties to those of the negative) compels then to the conception of *negative* charges extended through space, and thus, as it seems to me, leads to the nullification of the whole theory. For of what use is an atomical conception of electricity which cannot be subsequently worked out?

Geophysics. — "*On Frequencies of the mean daily cloudiness at Batavia.*" By Dr. J. P. van der Stok.

1. Since 1880 hourly observations of the cloudiness of the sky have been published by the Observatory at Batavia; if the daily means calculated from these records are arranged in groups, a frequency-table (Table I) is obtained which enables us to form a clear idea of the way in which the climate is affected by this highly important climatological factor.

From this Table it appears that, whilst northerly climates are characterized by a great number of cases in which the sky is entirely overcast or quite free from clouds (principally in April and September), these extreme values rarely occur at Batavia.

Only once in 26 years or in 9500 cases a serene sky lasting during 24 hours has been recorded and, taken over the whole year, the number of days during which the sky was entirely covered only amount to 1.4 °/₀ and, even in full West-Monsoon, to hardly more than 4 °/₀.

Furthermore Table I exhibits the fact that, notwithstanding the great number of records, irregularities still occur to a considerable extent and the sums taken over the whole year clearly demonstrate that extreme care must be taken in adding together frequency-series of different kinds, which may lead to irregularities of the most peculiar description in the curve of distribution; and these irregularities are by no means eliminated by a greater number of data.

In order to eliminate these irregularities three natural groups have

TABLE I. Frequencies of the mean daily cloudiness as recorded at Batavia 1880—1905.

Cloudiness	Jan.	Febr.	March	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Total
0	—	—	—	—	—	—	—	1	—	—	—	—	1
0 5	—		—	—	3	10	4	4	2	2	—	—	25
1	1	—	1	2	10	11	18	19	9	9	1	—	81
1.5	2	2	2	6	10	26	39	33	21	14	4	—	164
2	5	4	1	7	36	39	52	59	37	31	9	4	284
2.5	2	7	13	25	34	52	52	75	49	36	13	4	362
3	7	7	15	35	53	52	69	84	69	44	21	5	461
3.5	5	10	30	49	70	54	**78**	**85**	88	52	30	13	564
4	9	10	33	45	70	66	71	76	**89**	58	33	24	584
4.5	29	24	40	59	**80**	**68**	62	74	78	**84**	37	31	666
5	30	23	39	64	80	55	80	58	57	63	48	33	650
5.5	39	25	70	76	60	58	56	42	62	60	62	53	663
6	51	34	73	79	58	49	46	52	38	58	62	74	674
6.5	68	69	68	**88**	62	44	45	32	47	60	**79**	53	715
7	61	77	**93**	67	43	43	29	42	38	56	64	64	677
7.5	78	86	84	50	50	45	24	33	33	56	76	93	708
8	100	81	77	51	39	42	23	12	19	31	78	**102**	655
8.5	**101**	90	66	36	24	33	28	13	16	40	62	94	603
9	90	**94**	51	29	10	16	18	7	21	32	52	67	487
9.5	93	66	39	10	8	14	6	3	6	14	38	62	359
10	35	25	11	2	1	3	6	2	1	6	11	30	133
Total	806	734	806	780	806	780	806	806	780	806	780	806	9496

been formed as shown in Table II; in these series irregularities still occur, but by far the greater part have disappeared and they furnish good material for the application and the testing of frequency-formulae.

For this purpose two alterations have to be made: in the first place the scale value has to be altered so that the extreme limits are denoted, not by 0 and 10, but by ± 1, and consequently the origin of coordinates must be chosen in the middle between the limits;

TABLE II. Frequencies of the mean daily cloudiness, Batavia, 1880—1905.

Cloudiness	I East Monsoon	II Transition	III West-Monsoon	I East Monsoon	II Transition	III West-Monsoon	New scale values
0	1	—	—	—	—	—	—1.0
0.5	23	2	—	6	1	—	—0.9
1	67	13	1	17	4	—	—0.8
1.5	134	26	4	34	8	2	—0.7
2	223	48	13	56	15	6	—0.6
2.5	262	87	13	66	27	6	—0.5
3	327	115	19	82	36	8	—0.4
3.5	**375**	161	28	**94**	51	12	—0.3
4	372	169	43	93	53	18	—0.2
4.5	362	220	84	91	69	36	—0.1
5	330	214	86	83	68	37	0.0
5.5	278	268	117	70	84	50	0.1
6	243	272	159	61	86	68	0.2
6.5	230	**295**	190	58	**93**	81	0.3
7	195	280	202	49	88	86	0.4
7.5	185	266	257	47	84	110	0.5
8	135	237	283	34	75	120	0.6
8.5	114	204	**285**	29	64	**121**	0.7
9	72	164	251	18	52	107	0.8
9.5	37	101	221	9	32	94	0.9
10	13	30	90	3	10	38	1.0
Total	3978	3172	2346	1000	1000	1000	

this may be done by simply assuming the denotation as given in the last column of Table II.

In the second place the frequencies corresponding to the extreme limits must be excluded from the calculation because they must be considered as representing peculiar meteorological conditions and also because they cannot be taken as representing average values between ∓1.05 and ∓0.95 in the same sense as any other group.

Therefore, in calculating the constants of frequency-formulae, these extreme values are omitted and the remaining frequencies again reduced to a total of 1000.

2. In the first place the frequency-formula known as Type I of Prof. PEARSON's formulae finds an application:

$$u = \mathfrak{A}\left(1 + \frac{x}{p}\right)^a \left(1 - \frac{x}{q}\right)^b$$

which, for the assumed conditions and choice of origin, takes the simple form:

$$u = \mathfrak{A}\,(1 + x)^a\,(1 - x)^b \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

and can be regarded as a generalization of the condition that the function vanishes for $x = \pm 1$.

Its constants may be calculated from the following relations:

$$\mathfrak{A} = \frac{1}{2^{a+b+1}} \frac{\Gamma(a + b + 2)}{\Gamma(a + 1)\,\Gamma(b + 1)} \quad . \; . \; . \; . \; . \quad (2)$$

$$\frac{(\mu + 1)^{(n)}}{(\mu + 1)^{(n-1)}} = \frac{2\,(a + n)}{a + b + n + 1} \quad . \; . \; . \; . \; . \; . \quad (3)$$

where

$$(\mu + 1)^{(n)}\,\mu_n + n\,\mu_{n-1} + \frac{n(n-1)}{2\,!}\,\mu_{n-2} + \text{etc.}$$

and μ_n represents the mean of the n^{th} order.

As, besides $\mathfrak{A}$, by which the area of the curve is defined as equal to unity, only two constants appear in formula (1) as characteristics of the curve, it is sufficient to calculate the means of the first and second order μ_1 and μ_2.

Putting

$$p = 1 - \mu_1, \quad q = \frac{1 - \mu_2}{1 + \mu_1},$$

we find:

$$a + 1 = \frac{(2 - p)q}{2\,(p - q)}, \quad b + 1 = \frac{p\,q}{2\,(p - q)} \quad . \; . \; . \; . \quad (4)$$

This formula offers the advantage that, the constants a and b being known, a simple expression can be given for the situation of the maximum-value:

$$x_m = \frac{a - b}{a + b}.$$

In the second place we have to consider the expression in series-form proposed by the author in an earlier publication 1), which may be regarded as a generalized zonal function, modified according to the condition:

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1) These Proceedings Vol. X. (799—817).

$$u = 0 \text{ for } x = \pm 1.$$

$$u = \Sigma A'_n R_{n+2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

$$R_{n+2} = (x^2-1) R'_n = (x^2-1) \left[x^n - \frac{n(n-1)}{2.(2n+1)} x^{n-2} + \right.$$
$$\left. + \frac{n(n-1 (n-2) (n-3)}{2.4.(2n+1)(2n-1)} x^{n-4} - \text{etc.} \right]$$

$$A'_n = \beta \left[\mu_n - \frac{n(n-1)}{2.(2n+1)} \mu_{n-2} + \frac{n(n-1)(n-2)(n-3)}{2.4.(2n+1)(2n-1)} \mu_{n-4} - \text{etc.} \right] . \qquad (6)$$

$$\beta = - \frac{(2n+3)\ (2n+1)!\ (2n+1)!}{2^{2n+1}\ (n+2)!\ n!\ n!\ n!} . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

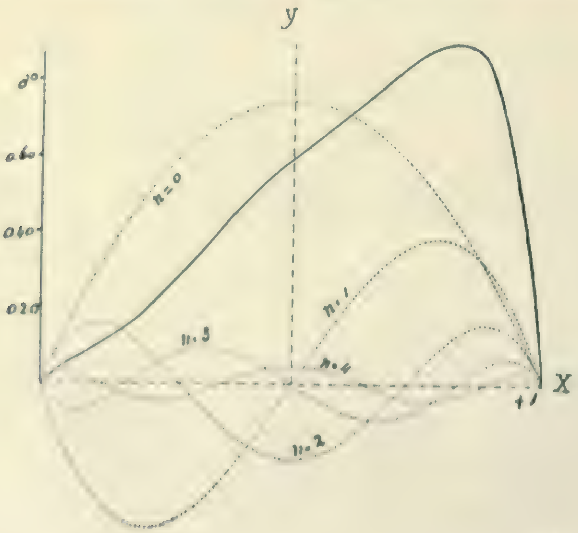
$$\mu_n = \int_{-1}^{+1} u x^n dx.$$

The use of the proposed series enables us to introduce more constants than two, which, in this case, is a decided advantage as the means of higher order necessarily decrease and, therefore, the convergency is assured.

For the position of the maximum-value however no definite expression can be derived from these formulae, and it has to be determined by approximative methods.

Values of the function R_{n+2} for $n = 0$ to $n = 4$ have been calculated and are given in Table X; for the first term, which remains the same for all curves, $A_0 R_2$ has been given instead of R_2.

The figure represents the way in which a frequency-curve (full



line) according to this formula is constructed out of its constituents (broken line) for the case:

$$A_1 = A_2 = A_3 = A_4 = 1,$$

so that the ordinates of the curve are found simply by taking together the 5 columns of Table X.

3. The following constants of formulae (1) and (5) are deduced from the data given in Table II (2nd part), the frequencies for a cloudiness 0 and 10 being omitted and the total reduced to 1000. For reasons to be given furtheron, the values of the A_n constants are not quite in conformity with the expression (6), the sign being inverted and the values divided by $n + 3$, so that;

$$(n + 3)\, A_n = - A'_n$$

I. East-Monsoon.

$$\begin{array}{lll}
\mu_1 = -0.0554 & A_1 = -0.0519 & \mathfrak{A} = 0.8416 \\
\mu_2 = +0.1690 & A_2 = -0.1017 & a = 1.3654 \\
\mu_3 = -0.0095 & A_3 = +0.1631 & b = 1.6428 \\
\mu_4 = +0.0631 & A_4 = -0.0650 &
\end{array}$$

II. Months of Transition.

$$\begin{array}{lll}
\mu_1 = 0.2136 & A_1 = +0.2003 & \mathfrak{A} = 0.7486 \\
\mu_2 = 0.1999 & A_2 = -0.0003 & a = 2.1470 \\
\mu_3 = 0.0921 & A_3 = +0.0069 & b = 1.0393 \\
\mu_4 = 0.0859 & A_4 = +0.0081 &
\end{array}$$

III. West-Monsoon.

$$\begin{array}{lll}
\mu_1 = 0.4545 & A_1 = +0.4261 & \mathfrak{A} = 0.4326 \\
\mu_2 = 0.3191 & A_2 = +0.3901 & a = 3.4001 \\
\mu_3 = 0.2173 & A_3 = +0.2584 & b = 0.6502 \\
\mu_4 = 0.1683 & A_4 = +0.1299 &
\end{array}$$

In the constants of either formula the differences characteristic for the different seasons are well marked.

4. In order to examine in how far the results of the computation by means of the frequency-formulae agree with the data, we have to integrate the expressions between the limits x and -1.

For the formula (5) in seriesform this offers no difficulty; from the differential equation:

$$(x^2 - 1)\frac{d^2 R_{n+2}}{dx^2} = (n + 2)(n + 1) R_{n+2}$$

we readily find:

$$I'_n = \int_{-1}^{x} R_{n+2}\, dx = \frac{(x^2-1)^2}{n+3} \cdot \frac{1}{n} \frac{dR'_u}{dx} \quad . \quad . \quad . \quad . \quad (8)$$

from which, the R'_n function being known, we easily derive the expressions (10). Formula (8) holds good for all values of n except $n=0$, in which case:

$$I'_0 = \frac{x^3-3x-2}{3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The A_n coefficients, calculated by formula (6) being comparatively large and the values computed by (8) small, it is desirable to omit the factor $(n+3)$ in (8) and (9) and to divide the expression for A_n by the same quantity; at the same time the sign of β, and therefore also the signs of (8) and (9), can be changed.

With these premises the integrals assume the form:

$$\left.\begin{aligned} I_0 &= x(1-x^2) + 2(1+x) \\ I_1 &= -(1-x)^2 \\ I_2 &= I_1 x \\ I_3 &= I_1\left(x^2-\frac{1}{7}\right) \\ I_4 &= I_1 x\left(x^2-\frac{1}{3}\right) = I_2\left(x^2-\frac{1}{3}\right) \end{aligned}\right\} \quad . \quad . \quad . \quad (10)$$

Numerical values of these integrals calculated for values of x increasing by 0.05 are given in Table IX; in the first column, which remains the same for curves of different description, instead of I_0 the product $A_0 I_0$ has been given.

Integrating formula (1) between the limits x and -1, we encounter the difficulty that, putting:

$$x = 2z - 1$$

and developing, we obtain the form:

$$\int_{-1}^{x} u\,dx = 2^{a+b+1}\,\mathfrak{A}\left[\frac{z^{a+1}}{a+1} - b\frac{z^{a+2}}{a+2} + \frac{b(b-1)}{2!}\frac{z^{a+3}}{a+3} - \text{etc.}\right]$$

which, evidently, for large values of z slowly converges, so that a considerable number of terms have to be taken into account if, as is necessary in our case, we desire to determine the values with an accuracy up to the third decimal.

Other forms of development are of course possible, but I have not succeeded in finding less laborious expressions.

5. As, owing to this difficulty, the computations necessary for the testing of the formulae had to be restricted, the frequencies of Table II have been aggregated between wider limits: Table III exhibits these frequencies reduced to a total of 1000; in the first part for all data, in the second part with the omission of frequencies for a cloudiness 0 and 10. It is this series which has to be compared with the results of the calculation.

TABLE III.

	I	II	III	I	II	III
−1.00 tot −0.75	23	5	0	23	5	0
−0.75 „ −0.55	90	23	8	90	23	8
−0.55 „ −0.35	148	63	14	149	64	15
−0.35 „ −0.15	187	104	30	188	105	31
−0.15 „ 0.05	174	137	73	175	138	76
0.05 „ 0.25	131	170	118	131	172	123
0.25 „ 0.45	107	181	167	107	183	174
0.45 „ 0.65	81	159	230	81	161	239
0.65 „ 0.85	47	116	228	47	117	237
0.85 „ 1.00	12	42	132	9	32	97

The results of the computation according to formula (5) are given in Table IV.

TABLE IV. I. East-Monsoon.

	A_1I_1	A_2I_2	A_3I_3	A_4I_4	A_0I_0 + total
−1.00 tot −0.75	0.0099	−0.0146	−0.0131	−0.0021	0.0231
−0.75 „ −0.55	0.0153	−0.0126	0.0004	0.0026	0.0917
−0.55 „ −0.35	0.0147	−0.0002	0.0151	0.0032	0.1520
−0.35 „ −0.15	0.0096	0.0128	0.0164	−0.0008	0.1781
−0.15 „ +0.05	0.0021	0.0196	0.0040	−0.0040	0.1708
+0.05 „ +0.25	−0.0060	0.0173	−0.0113	−0.0028	0.1433
+0.25 „ +0.45	−0.0126	0.0068	−0.0177	0.0015	0.1091
+0.45 „ +0.65	−0.0157	−0.0071	−0.0090	0.0037	0.0760
+0.65 „ +0.85	−0.0133	−0.0154	0.0079	0.0004	0.0447
+0.85 „ +1.00	−0.0040	−0.0067	0.0073	−0.0017	0.0169

TABLE IV. II. Transition.

	A_1I_1	A_2I_2	A_3I_3	A_4I_4	A_0I_0 + total
—1.00 tot —0.75	—0.0383	0.0000	—0.0006	0.0003	0.0044
—0.75 „ —0.55	—0.0591	0.0000	0.0000	—0.0003	0.0267
—0.55 „ —0.35	—0.0568	0.0000	0.0006	—0.0004	0.0625
—0.35 „ —0.15	—0.0372	0.0000	0.0007	0.0001	0.1037
—0.15 „ +0.05	—0.0079	0.0001	0.0002	0.0005	0.1420
+0.05 „ +0.25	0.0233	0.0001	—0.0005	0.0003	0.1693
+0.25 „ +0.45	0.0487	0.0000	—0.0007	—0.0002	0.1789
+0.45 „ +0.65	0.0606	0.0000	—0.0004	—0.0005	0.1638
+0.65 „ +0.85	0.0514	0.0000	0.0003	0.0000	0.1168
+0.85 „ +1.00	0.0154	0.0000	0.0003	0.0002	0.0319

TABLE IV. III. West-Monsoon.

	A_1I_1	A_2I_2	A_3I_3	A_4I_4	A_0I_0 + total
—1.00 tot —0.75	—0.0816	0.0561	—0.0208	0.0043	0.0010
—0.75 „ —0.55	—0.1257	0.0484	0.0007	—0.0053	0.0042
—0.55 „ —0.35	—0.1208	0.0007	0.0241	—0.0063	0.0168
—0.35 „ —0.15	—0.0790	—0.0493	0.0257	0.0016	0.0391
—0.15 „ +0.05	—0.0168	—0.0754	0.0064	0.0079	0.0712
+0.05 „ +0.25	0.0495	—0.0664	—0.0179	0.0056	0.1169
+0.25 „ +0.45	0.1035	—0.0260	—0.0281	—0.0029	0.1776
+0.45 „ +0.65	0.1289	0.0271	—0.0143	—0.0074	0.2384
+0.65 „ +0.85	0.1093	0.0591	0.0126	—0.0008	0.2453
+0.85 „ +1.00	0.0328	0.0256	0.0115	0.0033	0.0892

Table V shows the differences between the results of the observation *O* (Table III 2nd part) and of the computation *C* (Table IV last column).

TABLE V. $\Delta = O - C$, formula in seriesform.

	I. East-Monsoon	II. Transition	III. West-Monsoon.
—1.00 tot —0.75	0	1	—1
—0.75 „ —0.55	—2	—4	4
—0.55 „ —0.35	—3	1	—2
—0.35 „ —0.15	10	1	—8
—0.15 „ 0.05	4	—4	5
0.05 „ 0.25	—12	3	6
0.25 „ 0.45	—2	4	—4
0.45 „ 0.65	5	—3	1
0.65 „ 0.85	2	0	—8
0.85 „ 1.00	—2	0	8
$\sqrt{\frac{\Delta^2}{n}}$	5.57	2.63	5.39

The question whether or not PEARSON's formula (1) leads to an equally satisfactory result can be readily answered by supposing formula (1) to be expanded according to formula (5). Then, of course, the coefficients A_1 and A_2 will be the same whether calculated directly or with the help of a and b and, as the fourth term plays an unimportant part, all depends upon the third term which is determined by the mean of the third order μ_3.

If by means of (3) we calculate μ_3 from a and b, we find:

		observed	calculated by (3)		observed	calculated by (3)
East-Monsoon	$\mu_3 =$	—0.0095	—0.0225	$\mu_4 =$	0.0631	0.0641
Transition	,, $=$	0.0921	0.0902	,, $=$	0.0859	0.0856
West-Monsoon	,, $=$	0.2173	0.3219	,, $=$	0.1683	0.1917

From this we may conclude that, for the months of transition formula (1) will lead to excellent results; for the West-Monsoon the agreement will be satisfactory; but for the East-Monsoon rather large discrepancies are to be expected.

TABLE VI. $\Delta = O-C$, formula Pearson.

	I East-Monsoon	II Transition	III West-Monsoon
—1.00 tot —0.75	—13	— 1	0
— 0.75 „ — 0.55	— 1	— 4	4
—0.55 „ —0.35	12	3	0
—0.35 „ —0.15	25	3	7
—0.15 „ 0.05	6	— 2	0
0 05 „ 0 25	—25	2	— 2
0.25 „ 0.45	—18	2	— 7
0.45 „ 0.65	— 1	— 5	12
0.65 „ 0.85	10	1	4
0.85 „ 1.00	5	1	— 4
$\sqrt{\frac{\Delta^2}{n}}$	14.32	2.72	5.42

The differences given in Table VI confirm this expectation as well as the computation of the position of the maximum-value.

Position of maximum-values.

	Observed	Calculated	
	Table II.	form. Pearson	form. series
East-Monsoon	—0.25	—0.09	— 0.20
Transition	0.30	0.35	0.35
West-Monsoon	0.65	0.90	0.65

The use of frequency-formulae with two constants will, therefore, give satisfactory results only in those cases where the curve is of a comparatively simple construction or if, by chance, μ_3 (or A_3) as calculated by means of a and b, are approximately equal to the observed values.

Moreover, as the constants appear in exponential form, it will be difficult to calculate Tables for the function and its integrals as p and q may assume all possible values and occur in an infinite number of combinations.

Constants for every month computed according to both formulae from the data of Table I with the omission of the extreme values are given in Tables VII and VIII.

TABLE VII.
Constants of formula (5).

	A_1	A_2	A_3
January	0.4293	0.4118	0.3514
February	0.4247	0.3957	0.2653
March	0.2962	0.0847	—0.0207
April	0.1481	—001385	—0.0792
May	0.0114	—0.1572	0.0609
June	—0.0003	—0.1939	0.0988
July	—0.0672	—0.0758	0.1769
August	– 0.1330	—0.1093	0.2607
September	—0.0548	—0.1509	0.2963
October	0.0724	—0.0735	0.0885
November	0.2747	0.0961	0.0425
December	0.3795	0.2530	0.1355

TABLE VIII.
Constants of formula Pearson, Type I.

	$\mathfrak{A}$	a	b
January	0.420	3.242	0.577
February	0.436	3.278	0.611
March	0.656	3.041	1.101
April	0.880	2.671	1.670
May	0.922	1.824	1.756
June	0.924	2.049	2.050
July	0.798	1.225	1.568
August	0.831	1.439	2.246
September	0.894	1.645	1.974
October	0.813	1.573	1.204
November	0.664	2.475	0.900
December	0.534	3.484	0.900

TABLE IX. Values of I_n.

x	$A_0 I_0$	$n=1$	$n=2$	$n=3$	$n=4$
—1.00	0.0000	0.0000	0.0000	0.0000	0.0000
—0.95	0.0018	—0.0095	0.0090	—0.0072	0.0051
—0.90	0.0073	—0.0361	0.0325	—0.0241	0.0155
—0.85	0.0160	—0.0770	0.0655	—0.0446	0.0255
—0.80	0.0280	—0.1296	0.1037	—0.0644	0.0318
—0.75	0.0430	—0.1914	0.1436	—0.0803	0.0329
—0.70	0.0608	—0.2601	0.1821	—0.0903	0.0285
—0.65	0.0812	—0.3335	0.2168	—0.0933	0.0193
—0.60	0.1040	—0.4096	0.2458	—0.0889	0.0066
—0.55	0.1291	—0.4865	0.2676	—0.0777	—0.0082
—0.50	0.1563	—0.5625	0.2813	—0.0602	—0.0234
—0.45	0.1853	—0.6360	0.2862	—0.0379	—0.0374
—0.40	0.2160	—0.7056	0.2822	—0.0121	—0.0489
—0.35	0.2482	—0.7700	0.2695	0.0147	—0.0568
—0.30	0.2818	—0.8281	0.2484	0.0438	—0.0604
—0.25	0.3164	—0.8789	0.2197	0.0707	—0.0595
—0.20	0.3520	—0.9216	0.1843	0.0948	—0.0541
—0.15	0.3884	—0.9555	0.1433	0.1150	—0.0445
—0.10	0.4253	—0.9801	0.0980	0.1303	—0.0317
—0.05	0.4625	—0.9950	0.0498	0.1397	—0.0165
0.00	0.5000	—1.0000	0.0000	0.1429	0.0000
0.05	0.5375	—0.9950	—0.0498	0.1397	0.0165
0.10	0.5748	—0.9801	—0.0980	0.1303	0.0317
0.15	0.6117	—0.9555	—0.1433	0.1150	0.0445
0.20	0.6480	—0.9216	—0.1843	0.0948	0.0541
0.25	0.6836	—0.8789	—0.2197	0.0707	0.0595
0.30	0.7183	—0.8281	—0.2485	0.0438	0.0604
0.35	0.7518	—0.7700	—0.2695	0.0147	0.0568
0.40	0.7840	—0.7056	—0.2822	—0.0121	0.0489
0.45	0.8147	—0.6360	—0.2862	—0.0379	0.0374
0.50	0.8438	—0.5625	—0.2813	—0.0602	0.0234
0.55	0.8709	—0.4865	—0.2676	—0.0777	0.0082
0.60	0.8960	—0.4096	—0.2458	—0.0889	—0.0066
0.65	0.9189	—0.3335	—0.2168	—0.0933	—0.0193
0.70	0.9393	—0.2601	—0.1821	—0.0903	—0.0285
0.75	0.9570	—0.1914	—0.1436	—0.0803	—0.0329
0.80	0.9720	—0.1296	—0.1037	—0.0644	—0.0318
0.85	0.9840	—0.0770	—0.0655	—0.0446	—0.0255
0.90	0.9928	—0.0361	—0.0325	—0.0241	—0.0155
0.95	0.9982	—0.0095	—0.0090	—0.0072	—0.0051
1.00	1.0000	0.0000	0.0000	0.0000	0.0000

TABLE X. Values of the function R_{n+2}.

x	A_1R_2	$n=1$	$n=2$	$n=3$	$n=4$
1.00	0.0000	0.0000	0.0000	0.0000	0.0000
—0.95	0.0731	—0.0926	0.0685	—0.0439	0.0254
—0.90	0.1425	—0.1710	0.1159	—0.0652	0.0311
—0.85	0.2081	—0.2359	0.1450	—0.0693	0.0244
—0.80	0.2700	—0.2880	0.1584	—0.0609	0.0110
—0.75	0.3281	—0.3281	0.1586	—0.0439	—0.0048
—0.70	0.3825	—0.3570	0.1479	—0.0219	—0.0199
—0.65	0.4331	—0.3754	0.1285	0.0023	—0.0321
—0.60	0.4800	—0.3840	0.1024	0.0263	—0.0402
—0.55	0.5231	—0.3836	0.0715	0.0484	—0.0426
—0.50	0.5625	—0.3750	0.0375	0.0670	—0.0424
—0.45	0.5981	—0.3589	0.0020	0.0811	—0.0370
—0.40	0.6300	—0.3360	—0.0336	0.0902	—0.0281
—0.35	0.6581	—0.3071	—0.0680	0.0940	—0.0167
—0.30	0.6825	—0.2730	—0.1001	0.0924	—0.0039
—0.25	0.7031	—0.2344	—0.1289	0.0858	0.0092
—0.20	0.7200	—0.1920	—0.1536	0.0746	0.0217
—0.15	0.7331	—0.1466	—0.1735	0.0595	0.0324
—0.10	0.7425	—0.0990	—0.1881	0.0414	0.0406
—0.05	0.7481	—0.0499	—0.1970	0.0213	0.0458
0.00	0.7500	0.0000	—0.2000	0.0000	0.0476
0.05	0.7481	0.0499	—0.1970	—0.0213	0.0458
0.10	0.7425	0.0990	—0.1881	—0.0414	0.0406
0.15	0.7331	0.1467	—0.1735	—0.0595	0.0324
0.20	0.7200	0.1920	—0.1536	—0.0746	0.0217
0.25	0.7031	0.2344	—0.1289	—0.0858	0.0092
0.30	0.6825	0.2730	—0.1001	—0.0924	—0.0039
0.35	0.6581	0.3071	—0.0680	—0.0940	—0.0167
0.40	0.6300	0.3360	—0.0336	—0.0902	—0.0281
0.45	0.5981	0.3589	0.0020	—0.0811	—0.0370
0.50	0.5625	0.3750	0.0375	—0.0670	—0.0424
0.55	0.5231	0.3836	0.0715	—0.0484	—0.0436
0.60	0.4800	0.3840	0.1024	—0.0263	—0.0402
0.65	0.4331	0.3754	0.1285	—0.0023	—0.0321
0.70	0.3825	0.3570	0.1479	0.0219	—0.0199
0.75	0.3281	0.3281	0.1586	0.0439	—0.0048
0.80	0.2700	0.2880	0.1584	0.0609	0.0110
0.85	0.2081	0.2359	0.1450	0.0693	0.0244
0.90	0.1425	0.1710	0.1159	0.0652	0.0311
0.95	0.0731	0.0926	0.0685	0.0439	0.0254
1.00	0.0000	0.0000	0.0000	0.0000	0.0000

Mathematics. — *"On fourdimensional nets and their sections by spaces."* (Third part.) By Prof. P. H. SCHOUTE.

The net (C_{16}).

1. In the first part of this investigation we have found that the net (C_{16}) of cells $C_{16}^{(2\sqrt{2})}$ is formed out of three equally strongly developed groups of homothetic cells $C_{16}^{(2\sqrt{2})}$, *one* group of *erect* cells $C_{16}^{(2\sqrt{2})}$ polarly inscribed in eightcells $C_8^{(4)}$ and *two* groups of *inclined* cells $C'^{(2\sqrt{2})}_{16}$ and $C''^{(2\sqrt{2})}_{16}$ bodily inscribed in eightcells $C_8^{(2)}$, namely the *positive* group and the *negative* one. If we restrict ourselves once more, with respect to this net, to the sections by spaces normal to one of the four different axes of one of the sixteencells, it is evident from the table of connections between these different axes given in the first part (p. 544) — if we bear in mind that the three groups of cells of the net are equivalent — that we have only to consider three series of parallel intersecting spaces, viz. those normal to one of the axes OR_8, OF_8, OK_8 of the circumscribed eightcells. In these three cases, corresponding successively to the fifth, the fourth, and the third line of the quoted table, we find indeed for the erect sixteencells series of spaces normal to OE_{16}, OK_{16} and OF_{16}, whilst the first of the three cases provides us, for the inclined sixteencells, with a series of spaces normal to OR_{16}. So all in all we have to bring to light three different threedimensional space-fillings and their transformation connected with a parallel motion of the intersecting space. But in order to do this we have to consider more than the four usual series of intersecting spaces respectively normal to an axis OE_{16}, OK_{16}, OF_{16}, OR_{16}; for the spaces normal to OK_8 presenting themselves in the last of the three cases are not normal to any one of the four axes of the *inclined* sixteencells but to the line connecting the centre of one of these cells with the point characterized by the coordinates (3, 1, 1, 1) with respect to the system of coordinates with the four axes OE_{16} of that cell as axes. So all in all we have to deal with five series of parallel intersecting spaces which may be characterized by the symbols (1,0,0,0), (1,1,0,0), (1,1,1,0), (1,1,1,1), (3,1,1,1), as they are always normal to the diameter of the cell passing through the point the coordinates of which with respect to the axes OE_{16} of the cell are given by the corresponding symbol.

2. In the same way as we have done this in our second com-

munication for the six series of parallel sections of the eightcell we indicate the results of the intersection of a single sixteencell $C_{16}^{(2\sqrt{2})}$ in two different manners. A first plate will give the projections of the limiting elements of the sixteencell on the diameter normal to the intersecting spaces, which will enable us to deduce the sections from it tabularly; a second plate will give the sections themselves in parallel perspective, included in the sections with the polarly circumscribed $C_8^{(4)}$ or the bodily circumscribed $C_8^{(2)}$. Moreover a third plate will contain two groups of diagrams, the first of which will elucidate the manner of deduction of the projections given on plate I, whilst the second is concerned with the space-fillings obtained by the intersection of the net (C_{16}). In order to facilitate the survey of these space-fillings we deviate from the way followed in the second communication and treat together the more or less regular space-fillings presenting themselves here, instead of joining each of them separately to the corresponding generating three series of intersecting spaces.

We now first consider the four diagrams of the first group of plate III dominating the deduction of the projections of plate I. In fig. 1 we once more show how the inclined cell $C_{16}^{(2\sqrt{2})}$, indicated by its vertices only, is inscribed in the cell C_8^2. If we indicate by A, B, C, D the vertices of one of the sixteen limiting bodies, by A', B', C', D' the opposite ones, the sixteen limiting tetrahedra are

		$A'B'CD$		
	$A'BCD$	$A'BC'D$	$AB'C'D'$	
$ABCD$	$AB'CD$	$A'BCD'$	$A'BC'D'$	$A'B'C'D'$
	$ABC'D$	$AB'C'D$	$A'B'CD'$	
	$ABCD'$	$AB'CD'$	$A'B'C'D$	
		$ABC'D'$		

Of these five groups of 1, 4, 6, 4, 1 tetrahedra those of the first, the third, and the fifth groups are inscribed in the eight limiting cubes of the eightcell, whilst the four vertices of each of the tetrahedra of the second and the fourth group always split up with reference to two opposite limiting cubes of the eightcell into one vertex and three vertices.

With reference to the system of coordinates $O(Y_1, Y_2, Y_3, Y_4)$ of the four diagonals AA', BB', CC'', DD' already used in the first communication the five series of parallel sections are characterized by the symbols (1, 0, 0, 0), (1, 1, 0, 0), (1, 1, 1, 0), (1, 1, 1, 1), (3, 1, 1, 1) mentioned above, from which can be deduced that the octuple of vertices of the sixteencell projects itself on the chosen axis of projection in these five cases in arrangements indicated by (1, 6, 1), (2, 4, 2), (3, 2, 3), (4, 4), (1, 3, 3, 1). Of these five cases the first and the fourth are evident by themselves; so the parts of plate I bearing the headings (1, 0, 0, 0) OE_{16} and (1, 1, 1, 1) OR_{16} can be understood immediately. The three other cases can be explained by the three following diagrams, a common characteristic of which is that the eight vertices of the sixteencell have been obtained by starting from the cube that is found by intersecting the eightcell of fig. 1 by the central space normal to AA', by splitting up the eight vertices of that cube into the two sets of vertices of bodily inscribed tetrahedra and by erecting normals on the space bearing that cube — i. e. by drawing in the diagram in parallel perspective lines parallel to AA'' — the length of which is equal to $\frac{1}{2} AA''$, in the vertices of one of the tetrahedra to one side and in the vertices of the other tetrahedron to the opposite side. This representation of the cube with the two quadruples of points $ABCD$, $A'B'C''D'$ has been repeated in three different positions by a motion parallel to itself from left to right and from above to below over the same distance, which gives rise to the three diagrams 2, 3, 4 which we will now examine one after another.

In fig. 2 the eight vertices of the sixteencell have been projected on to the line $F_8F''_8$, joining the midpoints of two opposite edges of the cube and forming therefore an axis OF_8 of the eightcell; on this axis the vertices A, B project themselves in F_8, the vertices C, D, C', D' in O and the vertices A', B' in F''_8. We find again here that the axis OF_8 of the eightcell is at the same time an axis OK_{16} of the bodily inscribed sixteencell, as F_8 is the midpoint of AB, and deduce now from the arrangement (2, 4, 2) of the projections of the vertices all that is indicated on plate I under the heading (1, 1, 0, 0) OK_{16}.

In fig. 3 the centres of gravity F_{16}, F''_{16} of the opposite faces ABC, $A'B'C''$ have been determined, and the axis OF_{16} joining these points forms the axis of projection. Then the three vertices A, B, C project themselves in F_{16}, the two vertices D, D' in O, the three vertices A', B', C'' in F_{16}. From the arrangement (3, 2, 3) can then be deduced what appears in plate I under the heading (1, 1, 1, 0) OF_{16}.

In fig. 4 the diagonal $D''D'''$ of the cube, forming an axis OK_8 of the eightcell, appears as axis of projection. Here the projection of the eight vertices of the sixteencell on that line $D''D'''$ is found in the easiest way by projecting these points first on to the space of the cube with the diagonal $D''D'''$ and by repeating this for the eight projections obtained with respect to the line $D''D'''$. For, the projections of the eight vertices of the sixteencell on to the space of the cube are the vertices of that cube, and these project themselves on $D''D'''$, if this line is divided by P and P' into three equal parts, according to the arrangement (1, 3, 3, 1) in the points D'', P, P', D'''. From this arrangement (1, 3, 3, 1) of the vertices can be deduced immediately what appears on plate I under the heading (3, 1, 1, 1) OK_8.

For each of the five cases considered we repeat under the heading "type" the manner in which the four couples of opposite vertices of the eightcell project themselves on the different axes.

3. We now proceed to the description of the sections, represented in parallel perspective on plate II, of the erect $C_{16}^{(2\sqrt{2})}$ and its envelope $C_8^{(4)}$ on one side, and the inclined $C''^{(2\sqrt{2})}_{16}$ and $C'''^{(2\sqrt{2})}_{16}$ and their envelopes $C_8^{(2)}$ on the other. The sections of the C_{16} can be deduced from the tables of projection of plate I, those of the circumscribed $C_8^{(4)}$ and $C_8^{(2)}$ have already been given on plate II of the second communication.

By two thick vertical lines *this* plate II is divided into three parts, respectively related to sections normal to OR_8, normal to OF_8, normal to OK_8. Each of these three parts is divided by a thin vertical line into two columns; of these two columns the lefthand one always contains three sections of erect sixteencells, the righthand one five or more sections of inclined sixteencells. We now consider separately each of the six columns so formed.

Sections normal to OR_8.

a. *Erect cells.* This case is the simplest of all. If by a motion parallel to itself of the intersecting space normal to the axis OE_{16} of $C_{16}^{(2\sqrt{2})}$ the point of intersection of that space with that axis moves from one of the two vertices situated on that axis to the other, the section with the circumscribed $C_8^{(4)}$ remains a cube with edge four and the section with the inscribed $C_{16}^{(2\sqrt{2})}$ itself, which is always a regular octahedron, increases in size from a point, the centre of the cube, to the inscribed octahedron with edge $2\sqrt{2}$ and then it passes through the same stadia in inverse order. Of the three diagrams the second represents an intermediate stadium, in which the edge of the octahedron is $\sqrt{2}$.

b. *Inclined cells.* If the point of intersection of the intersecting space normal to the axis OR_{16} of $C_{16}^{(2\sqrt{2})}$ with this axis describes this axis completely, the section with the bodily circumscribed $C_8^{(2)}$ remains a cube with edge two, whilst the section with the inscribed $C_{16}^{(2\sqrt{2})}$, always a tetrahedron truncated at the vertices and at the edges, transforms itself from a right tetrahedron to a left one in the manner shown by the five diagrams. In the third of the five we recognize the semiregular body (with regular faces) forming the combination of cube and octahedron in equilibrium, whilst the form represented by the second and the fourth show how this combination is formed out of the right tetrahedron and passes into the left one [1]).

Sections normal to OF_8.

a. *Erect cells.* Here a difference arises with respect to the fraction indicating the position of the intersecting space, according as the line through O normal to the intersecting space is considered either as an axis OK_{16} of the inscribed $C_{16}^{(2\sqrt{2})}$ or as an axis OF_8 of the circumscribed $C_8^{(4)}$. Therefore to each of the three diagrams presenting themselves here correspond two fractions, one below at the righthand side referring to the axis OK_{16}, another above at the lefthand side referring to the axis OF_8. If the point of intersection of the intersecting space with the axis OF_8 of $C_8^{(4)}$ describes this axis completely, the height of the rectangular parallelopipedon forming the section with $C_8^{(4)}$, the base of which is a square with side four, increases from nought to $4\sqrt{2}$ and then again decreases to nought. But only at the moment that this height is increased to $2\sqrt{2}$ does the polarly inscribed $C_{16}^{(2\sqrt{2})}$ begin to be cut. So we find in the three cases, where the height is respectively $2\sqrt{2}$, $3\sqrt{2}$, $4\sqrt{2}$ and the fractions above to the left are $\frac{2}{8}, \frac{3}{8}, \frac{4}{8}$, for the fractions below to the right $0, \frac{1}{4}, \frac{2}{4}$ and for the sections of $C_{16}^{(2\sqrt{2})}$ an edge, a cube covered at two opposite faces by square pyramids, a square double-pyramid.

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[1]) For the sake of clearness the limiting elements of the section of the cell C_{16} situated in the faces of the section of the enveloping box C_8 have been brought to the fore by indicating the vertices situated in *all* the faces of that envelope as black points, and by shading the faces of the section of the cell C_{16} situated in *visible* faces of that envelope.

b. *Inclined cells.* In the five cases corresponding to the fractions $0, \frac{1}{8}, \frac{2}{8}, \frac{3}{8}, \frac{4}{8}$ the section of the circumscribed $C_8^{(2)}$ is a rectangular parallelopipedon, the base of which is a square with side two, with a height $0, \frac{1}{2}\sqrt{2}, \sqrt{2}, \frac{3}{2}\sqrt{2}, 2\sqrt{2}$ successively. The sections of the inscribed $C_{16}^{(2\sqrt{2})}$ represented in the first, the third and the fifth of the five figures are equal to those of the preceding column and in the second and the fourth intermediate forms between these; in general the section can be characterized as a rectangular parallelopipedon with a square as base and upperplane, covered at these two faces by square pyramids, the faces of which have a determined inclination.

Sections normal to OK_8.

a. *Erect cells.* Here too, a difference presents itself as to the fractions, according as the diameter normal to the intersecting space is considered either as an axis OF_{16} or as an axis OK_8. If the point of intersection of the intersecting space with the axis OK_8 of $C_8^{(4)}$ describes that axis completely, the base of the prismatic section, the height of which remains four, transforms itself in the same manner as the section of a cube with edge four by a plane normal to a diagonal, and now at the moment that this base is increased to a triangle with side $4\sqrt{2}$ a face of the inscribed $C_{16}^{(2\sqrt{2})}$ appears in the intersecting space. So, to the fractions $\frac{4}{12}, \frac{5}{12}, \frac{6}{12}$ above to the left, correspond the fractions $0, \frac{1}{4}, \frac{2}{4}$ below to the right; so we find in the first diagram a triangle in a triangular prism, in the third a regular hexagonal double-pyramid in a regular hexagonal prism, in the second a form (12, 24, 14) bounded by two equilateral triangles, six isosceles triangles, six isosceles trapezia in a semiregular hexagonal prism regular as to the angles.

b. *Inclined cells.* The seven cases corresponding to the fractions $0, \frac{1}{12}, \frac{2}{12}, \ldots, \frac{6}{12}$ are all represented here. In the case corresponding to nought the section with $C_8^{(2)}$ is a line, here a vertical one, the section with $C_{16}^{(2\sqrt{2})}$ a point, here the upper extremity of that line. In the cases $\frac{1}{12}, \frac{2}{12}, \frac{3}{12}, \frac{4}{12}$ we find an irregular octahedron, inscribed in a triangular prism, bounded by two equilateral triangles of different size and two sets of three isosceles triangles of different form; the smaller of the two equilateral triangles is always inscribed in the upperplane of the prism, whilst the larger forms a normal section of the prism, successively at the height $\frac{3}{4}, \frac{2}{4}, \frac{1}{4}$, 0. Finally in the cases $\frac{5}{12}, \frac{6}{12}$ we find a semiregular hexagonal prism regular as to the angles and a regular one in which polyhedra (12, 24, 14) are inscribed, once more bounded by two equilateral triangles, six isosceles triangles and six isosceles trapezia. But here, in opposition to the form (12, 24, 14) found above, the two equilateral triangles instead of being homothetic have an opposite orientation.[1]

4. Before we pass to the generation of more or less regular spacefillings by intersecting the net (C_{16}) we wish to say a single word about the diagonal planes appearing in the sections of the cell C_{16} represented on plate II. In my communication "On groups of polyhedra with diagonal planes, derived from polytopes" published in these *Proceedings* of October (p. 277—290) it has been explained that any space intersecting C_{16} and not passing through one of the edges intersects this cell in a polyhedron with the property that through any edge of it passes one and only one diagonal plane, and that we only can obtain sections, through one or more edges of which pass two diagonal planes, if we choose an intersecting space passing through one or more edges of C_{16}. We have especially to show here

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[1] In the paper "Regelmässige Schnitte und Projectionen des Achtzelles u.s.w." (Regular sections and projections of the eightcell, the sixteencell, etc.", Verhandelingen of Amsterdam, first section, vol. II, N°. 2, 1894), I restricted myself principally to central sections; I only added incidentally a remark about the sections by spaces not passing through the centre. The figures 11 and 13 of that former paper, being not quite correct, should be replaced by the second figures of the third and fifth columns of plate II of this study.

why this particularity — as was already stated there — does not present itself in any of the sections of the four principal groups.

A mere inspection of plate II is sufficient to show, that *all* the sections of C_{16} represented there — not only those related to the axes OE_{16}, OK_{16}, OF_{16}, OR_{16} but also those of the last column — agree with one another in this, that any edge is situated in one and only one diagonal plane, moving parallel to itself if the intersecting space displaces itself parallelly. As an example we fix our attention on the figures of the fourth column, where a hexagon $MABNCD$ starts on half its journey as a line MN to end it as a lozenge $MANC$.

Now the reason, *why* no edge situated in two diagonal planes occurs here in the cases of sections by spaces containing edges of C_{16}, can be derived from plate I. It comes to this, that spaces through edges of C_{16}, not leaving that cell entirely on one side, do not present themselves for sections normal to OR_{16} or OF_{16}, that they pass through the centre O for sections normal to OE_{16} or OK_{16} and contain a face of C_{16} for sections under the heading $(3, 1, 1, 1) OK_8$. If the intersecting space — see fig. 2 of the communication of October — contains not only the edge AB but also the centre O of the cell, the two points of intersection S_{13} S_{24} coincide in O, and instead of two diagonal planes ABS_{13}, ABS_{24} we find only one diagonal plane ABO, containing also the edge $A'B'$ opposite to AB and therefore intersecting the section in a square; this happens in the cases of the last figures of the first and the third column of plate II, for the first column with each, for the third column with only one diagonal plane, represented horizontally. In the case of the last column corresponding to the fractional symbol $\frac{4}{12}$ the triangle OPQ forming the base of the section is a face of C_{16}; so through any side of this triangle passes only one diagonal plane.

5. In order to determine the threedimensional space-fillings generated by intersection of the net (C_{16}) we can follow different ways, some of which are of a more theoretic, others of a more practical character. Those of the first group correspond in this, that we deduce from the section of a determined C_{16} with the intersecting space how this space must affect the other cells of the net (C_{16}). So we can project the axes of all the cells, normal to the intersecting space, on the axis taken as axis of projection, and deduce from the fraction corresponding to the chosen C_{16} the fraction corresponding to any other cell of the net; this method has been applied to the

net C_8) in the second communication, and it can be of great service here, as the cells $C_8^{(2)}$ bodily circumscribed to the inclined cells C_{16} form a net (C_8). However, it often proves to be more practical to start from any section presenting itself, to hunt for other sections, possible in the position of the intersecting space under consideration, admitting a face agreeing in shape and in size with one of the faces of the chosen section, and to investigate if it is possible to arrive in this manner at a space-filling either by these two polyhedra only or by means of still more forms equally possible.

Space-fillings normal to OR_8. Let us imagine in threedimensional space a net of cubes with edge two, built up by cubes alternately white and black so as to form a threedimensional chessboard, with an infinite number of cubes, and let us describe in all white cubes a righthanded, in all black cubes a lefthanded tetrahedron. Then the interstitial spaces between these tetrahedra can be filled up by regular octahedra, forming with the tetrahedra the mixed net of tetrahedra and octahedra with common length of edge $2\sqrt{2}$. If we describe in all white cubes the tetrahedra truncated at vertices and edges of the second, in all black cubes the tetrahedra truncated at vertices and edges of the fourth of the five figures of the second column of plate II, the interstitial spaces can be filled up by regular octahedra of two different sizes, i.e. with edges $\frac{1}{2}\sqrt{2}$ and $\frac{3}{2}\sqrt{2}$. If we describe in *all* cubes the combination of cube and octahedron in equilibrium represented by the third of the five figures, the remaining interstitial spaces can be once more filled by regular octahedra of the same size, this time with the edge $\sqrt{2}$. These generally known results are obtained immediately by means of the method of juxtaposition, if we only bear in mind that two bodily inscribed sixteencells, the boxes $C_8^{(2)}$ of which have a limiting cube in common, are cut by any space normal to the space of that cube in polyhedra being one anothers mirror-image with respect to the plane of intersection as mirror, from which it ensues immediately that of the five figures of the second column the first and the fifth correspond to one another, also the second and the fourth, whilst the third stands for itself. By the juxtaposition, which comes here to the filling up of the interstitial spaces, we then find that the two extreme figures of the second column are to be combined with the two extreme figures of the first column, that the middle figure of the second column demands the middle figure of the first column, whilst the two remaining figures of the second column correspond to two intermediate sections with the fractions $\frac{1}{8}$ and $\frac{3}{8}$ of the first column, not represented here.

If the point O (fig. 5) is the centre and OR an axis OR_8 of one of the cells $C_8^{(2)}$ and we assume on the line which is to be considered as axis of projection a scale division with O as origin and half the edge of $C_8^{(2)}$ as unit, the vertices of the cells $C_8^{(2)}$ — and therefore also the centres of $C_8^{(4)}$ — project themselves into the points with a distance from O equal to an odd number of integers. If now the projection P of the intersecting space on to this axis lies between the origin and the point 1, and if $1—2x$ represents the distance OP, the section of all the cells $C_8^{(2)}$ corresponds to the fraction x, whilst both the series of $C_8^{(4)}$, the centres of which project themselves into the points -1 and $+1$, correspond to the fractions $y=\frac{x}{2}$ and $y'=\frac{x+1}{2}$. Now as the fraction x of a positively inscribed C_{16} inverts its sign and passes therefore into $1-x$, if this C_{16} is replaced by a negatively inscribed one, the fractions x and $1-x$ of the five figures of the second column belong together and to them correspond the fractions $\frac{1}{2}x$ and $\frac{1}{2}(x+1)$ of the first column. This result is in accordance with the preceding one; moreover it proves that it is preferable to say that the intermediate sections, not represented in the first column, corresponding to the second and the fourth figures of the second column, bear the fractional symbols $\frac{1}{8}$ and $\frac{5}{8}$.

It goes without saying that by the last method is indicated at the same time what the space-filling corresponding to an arbitrary value of x looks like; as this is immediately clear by itself we do not enter into details.

Space-fillings normal to OF_8. The result found above — that of the five figures of the second column those at the same distance from the middle one belong together — holds for this case too. This is proved easily, in a manner independent of preceding considerations, as follows. If PX_1, PX_2, PX_3, PX_4 (fig. 6) are the four edges of a $C_8^{(2)}$ meeting in a vertex P, if PQ and PR are the squares described on X_1PX_2 and X_3PX_4 and if F, G, O are the centres of these faces and of the eightcell, $FPGO$ is a square and the net (C_8), to which the cell $C_8^{(2)}$ belongs, projects itself on the plane of the square PR as a plane-filling of squares (fig. 7), whilst the intersecting space normal to the diagonal PR of the square projects itself in a normal to that line. We expressed this in the second communication by saying that the problem of the section of a four-dimensional polytope by a threedimensional space has lost here two of its dimensions. If now amongst the lines normal to the diagonal PR line a passes through R, line b passes through the points S_1, T_1 on the sides RS, RT for which $RS_1 = \frac{1}{4} RS$, $RT_1 = \frac{1}{4} RT$, and line c passes through the midpoints S_2, T_2 of RS, RT, then the position a of the intersecting space corresponds to the first and the fifth figure of the fourth column of plate II, the position b corresponds to the second and the fourth figure, the position c corresponds to the third one.

A second remark refers to the position of the sections obtained in the third and the fourth column. The first and the third figure of the third column are equal to the first and the fifth figure of the fourth column; also the middle figures of the two columns are equal. But there is a difference in position. In the figures of the third column the axis MN of period four is vertical, in the figures of the fourth column this axis MN is horizontal. This is not accidental. As both columns represent the sections with the polarly circumscribed $C_8'^{(4)}$ and the bodily circumscribed $C_2'^{(8)}$ in the same orientation, it proves that the axes MN of the sections of the erect sixteencells and those of any of the two groups of the inclined sixteencells are normal to one another, from which may be derived that the three axes MN of the sections of three sixteencells, any two of which belong to different groups, are normal to one another by twos. We verify this by proving that the axes MN of the sections of two inclined sixteencells of different kinds are normal to one another. Therefore we remark that the limiting spaces $P(X_1X_3X_4)$ and $P(X_2X_3X_4)$ of fig. 6 are parallel to OF — as the line GP parallel to OF lies in $P(X_3X_4)$ — and so the intersecting spaces normal to OF are normal to those limiting spaces of $C_2'^{(8)}$. As the sixteencells inscribed in $C_8'^{(2)}$ and in an adjacent $C_8^{(2)}$ are one another's mirror-image with respect to the limiting space common to the two eightcells, the sections of both the sixteencells with the intersecting space normal to that limiting space are one another's mirror-image with respect to the plane of intersection of intersecting space and limiting space, i.e. with respect to one of the vertical faces of the rectangular square prism that forms the section of C_8^2. As the axis MN of the figures of column four forms an angle of 45° with each of these four faces, it will be normal to its mirror-image.

In the first of the three cases — that of the first and the third figure of the third column — only one polyhedron appears, the square double-pyramid, the base of which is a square with side $2\sqrt{2}$, the height of which also is $2\sqrt{2}$. In the following way it is easily proved that this not entirely regular octahedron can form a space-filling by itself Let us consider a net of cubes with edge $2\sqrt{2}$ and divide each of these cubes into six equal square pyramids admitting as base one of the faces of that cube and as common vertex the centre of the cube; then the required net is obtained if we join together to a double-pyramid each pair of pyramids standing on the same base; according to the directions of the axes with period four of these pyramids this net consists of three equally strongly developed groups of polyhedra. We remark that the regular octahedron cannot fill space, but that we obtain a polyhedron that does fill space, as has just been proved, by compressing the regular octahedron in such a manner that the distances of the points of the surface from a plane through four of the six vertices are diminished to $\frac{1}{2}\sqrt{2}$ times the original value.

In the third of the three cases — i.e. in that of the middle figure of the five sections of column four — we have again to deal with only one polyhedron, viz. a cube with edge $\sqrt{2}$ bearing on two opposite faces a square pyramid with height $\frac{1}{2}\sqrt{2}$. We show easily that this body has the space-filling property as follows. Let us start from a net of cubes with edge $\sqrt{2}$ and suppose the centre of one of these cubes to be the origin of a rectangular system of coordinates the axes of which are parallel to the edges of the cube. Then let us divide into six equal square pyramids each cube the centre of which has for coordinates either only even or only odd multiples of $\sqrt{2}$, and join each of these pyramids to the adjacent cube; then the required space-filling is obtained. Of these the two figures 8^a and 8^b show the sections with planes $u=2k\sqrt{2}$ and $u=(2k+1)\sqrt{2}$, where u stands for any of the three coordinates: here have been indicated the fibres of the combination (10, 20, 12) running in the direction of the axis with period four, whilst sections normal to the axis are characterized by yearrings and medullary rays.

If we wish to treat in an analogous manner the second case — i.e. that of the second and the fourth figure of column four — we can start from a net of cubes with edge $2\sqrt{2}$. If we transform this net by assuming inside these cubes concentric and homothetic cubes with edge $\frac{3}{2}\sqrt{2}$ we find, by omitting the boundaries of the original cubes and producing the boundaries of the new ones, a mixed space-filling by cubes and rectangular parallelopipeda characterized by the triplets of edges $(1, 1, 1)$, $(3, 3, 3)$ and $(1, 1, 3)$, $(1, 3, 3)$ with $\frac{1}{2}\sqrt{2}$ as unit. By splitting up each of the cubes of the two sizes into six equal pyramids and joining these pyramids to the adjacent parallelopipeda we get the required space-filling. Here for clearness' sake the figures 9^a and 9^b show the sections corresponding to those of 8^a and 8^b.

In general the space-filling presenting itself here consists of two different polyhedra occurring in three different orientations; in two particular cases one finds however only one polyhedron occurring in three different positions.

Space-fillings normal to OK_8. — Here the problem of the determination of the section of the net (C_8') loses one dimension only; so the consideration of the section of a threedimensional net of cubes by a plane normal to a diagonal shows that three sections always go together whose characteristic fractions differ by $\frac{1}{3}$ from one another. Moreover we have still to bear in mind two things. First we have to observe that the three sections of $C_8'^{(2)}$ corresponding to the fractions a, $a+\frac{1}{3}$, $a+\frac{2}{3}$ do not always give three sections of a bodily inscribed sixteencell. If we assume for simplicity a to be situated between the limits 0 and $\frac{1}{3}$ we shall find three sections of $C_{16}'^{(2\sqrt{2})}$ if a lies between $\frac{1}{12}$ and $\frac{3}{12}$, i.e. in half the possible cases. In the second place we have to remember that each of two or three sections of sixteencells occurs in two different orientations, being one another's mirror-image with respect to the middle plane of the prism, section of the bodily circumscribed $C_8'^{(2)}$. If the intersecting space is normal to the line connecting the centre O of the chosen eightcell with the midpoint K_8 of its edge PQ, then we have only to consider two bodily adjacent eightcells of the net, the line joining the centres of which is equipollent to PQ, in order to see that these eightcells are intersected in two congruent prisms with common base, whilst the sections with the inscribed inclined sixteencells are symmetric figures with respect to that base If we consider difference in form only we have to deal therefore with two or three, if we also take into account difference in orientation we have to deal with four or six polyhedra.

If we deprive the problem of the intersection of the system of cells $C_8^{(4)}$ partially penetrating one another, polarly circumscribed to the erect sixteencells, of the one superfluous dimension, we find a system of cubes with edge four, the centres of which are the vertices of a net of cubes with edge two, whilst the edges are parallel to those of the cubes of the net. This system is then to be intersected by a plane normal to a diagonal. By means of a simple diagram we then find that to the three sections $a, a+\frac{1}{3}, a+\frac{2}{3}$ of the net $C_8^{(2)}$ correspond the six sections $\frac{a}{2}, \frac{a}{2}+\frac{1}{6}, \ldots, \frac{a}{2}+\frac{5}{6}$ of the system $C_8^{(4)}$. But of these six different sections of $C_8^{(4)}$ only two give rise to sections of erect sixteencells, viz. those the fractions of which lie between $\frac{2}{6}$ and $\frac{4}{6}$. So we get as the two most regular of the space-fillings presenting themselves here the two indicated by figures in heavy type in the following scheme:

In $C_8^{(4)}$ . . . $0, \frac{1}{6}, \frac{2}{6}, \mathbf{\frac{3}{6}}, \frac{4}{6}, \frac{5}{6}$	In $C_8^{(4)}$ . . . $\frac{1}{12}, \frac{3}{12}, \mathbf{\frac{5}{12}}, \mathbf{\frac{7}{12}}, \frac{9}{12}, \frac{11}{12}$
In $C_8^{(2)}$ . . . $0, \mathbf{\frac{1}{3}}, \mathbf{\frac{2}{3}}$	In $C_8^{(2)}$ . . . $\mathbf{\frac{1}{6}}, \mathbf{\frac{3}{6}}, \mathbf{\frac{5}{6}}$

Of these space-fillings the first consists of regular hexagonal double-pyramids (last figure of column five of plate II) and as to shape only one other form, an irregular octahedron (the octahedron of the sixth column with OPQ as base), whilst the second one is built up by three different bodies in that supposition. The diagrams 10 and 11 represent a projection of both on the base of the prisms forming the sections of the including eightcells.

From fig. 12, added partly to fill the page, which shows the sections of a cube by planes normal to an interior diagonal, can be deduced finally that the segments of lines PQ, RS, TU of the three figures of column five — and of the last three figures of column six — of plate II have the same length.

Physics. — *"On plaitpoint temperatures of the system water-phenol".* By A. Keesing. (Communicated by Prof. J. D. van der Waals).

According to observations by Lehfeldt, v. d. Lee, and Schreinemakers the system water-phenol possesses maximum pressure at low temperatures. So theoretically a minimum critical temperature was to be expected, but as water shows abnormal deviations in other respects, an elaborate investigation was desirable. In view of the high critical temperatures of the components (water 365°,0 according to Cailletet and Colardeau, or 364°,3 according to Battelli; phenol 419°,2 according to Radice) and the impossibility of using glass test-tubes (glass dissolves in water at such a high temperature) a conclusive investigation had not yet taken place as far as is known. Experimenting in a way similar to that indicated by Schamhardt [1]) I have succeeded in arriving at a preliminary result.

As for the determination of the plaitpoint temperature there was no need for me to regulate either the pressure or the volume I did not want a Cailletet tube, but used small closed test-tubes of *quartz*. This made it possible for me to use a vapour-jacket whose bottom was also glass, and which rested on asbestic iron gauze. In consequence of this one of the two nickelin wires, viz. the one used by Schamhardt to heat his boiling-liquid, could be dispensed with, and replaced by a Bunsen burner. The second wire, which enabled him to prevent satisfactorily the radiation at temperatures between 200° and 300°, proved insufficient for temperatures between 350° and 400°. A second layer of asbestos round the wire gave some improvement, but the radiation appeared to be completely prevented only when I placed a glass cylindre silvered on the inside, in which two slits were left free for reading, round the vapour-jacket, which had been thus wrapped up. This cylindre of a diameter 5 centimeters larger than that of the jacket, was shut off by means of asbestos wool on the upper and the lower side.

It was not without difficulty that we found a boiling-liquid, for in the Phys. Chem. tables of Landolt-Börnstein no boiling-liquids are given above 360°. I used *benzidine*, an inactive substance, which boils at 1 atm. pressure at ± 400° with colourless vapour. We have, however, to bear in mind:

1. that chemically pure benzidine be used, because impure benzidine boils irregularly, and covers the vapour-jacket, the quartz tube, and the thermometer with a tough, tarry layer, which prevents

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[1]) H. C. Schamhardt. Isotherms of mixtures of benzene and aether. Thesis for the doctorate p. 12—16.

the observation and which I could only remove partially by boiling long with water and benzene,

2. that the substance be boiled under nitrogen, as pure benzidine is soon contaminated by the oxygen from the air,

3. that superheating, which causes the liquid benzidine at times to rise $1^1/_2$ decimeter in the jacket, be prevented by a good quantity of glass-wool.

When benzidine was used, a cooler was not wanted, the vapour condensing in the narrowed part of the vapour-jacket.

The benzidine being heated under nitrogen, I required a nitrogen reservoir. For this purpose a 100 L. flask was used, which was filled with nitrogen obtained from a saturate solution of equal units of weight of potassium nitrite and ammonium chloride. When the reservoir had once been filled, the nitrogen could be expelled from the flask by the admission of water, and be conducted through a drying apparatus to the vapour-jacket. The pressure in the reservoir was measured by a manometer.

The experiments proper began with the filling of the nitrogen reservoir. The phenol and water were weighed in the required ratio, and heated with a spirit lamp. The temperatures at which water and phenol do not mix appeared then to be exceeded, and a homogeneous liquid was formed. A thick-walled quartz tube closed on one side, and drawn out capillarly on the other side in the voltaic arc was now heated in the free flame, and the air expelled under the phenol water solution; the liquid now rose in the tube which was filled for more than $^1/_3$, and then fused together in the voltaic arc. The quartz appeared then to be a very suitable material. It is as clear and transparent as glass, but, when hot, may be cooled in cold water without bursting; it may be heated in a free flame, and is proof to high pressures, as the critical pressure of water, viz. 200 atm. Protective measures proved to have been most likely superfluous.

Thermometer and quartz tube were fastened by means of copper wires in a hole of the glass tube which pierces the airtight rubber stopper of the vapour-jacket. The apparatus were filled with nitrogen, the pressure in the boiling vessel was reduced to about 30 cm., the gas-burner lighted, and every five minutes a lamp was inserted of the resistance, by the aid of which the current required to check radiation was regulated. After an hour the thermometer indicated about 350°. As soon as this temperature had become constant, which also appeared from the fact that the boiling phenomena stopped in the quartz tube, nitrogen was gradually admitted. The meniscus began then to become gradually fainter. The incandescent lamps placed behind the slit made the inner wall of the quartz tube look like a streak of light, in which the meniscus made a notch. By moving the eye to and fro in front of this notch I could ascertain the presence of the liquid mirror as long as possible. The temperature at which the meniscus disappeared, was noted down; also the temperature at which the liquid mirror returned on decrease of pressure in the vapour-jacket.

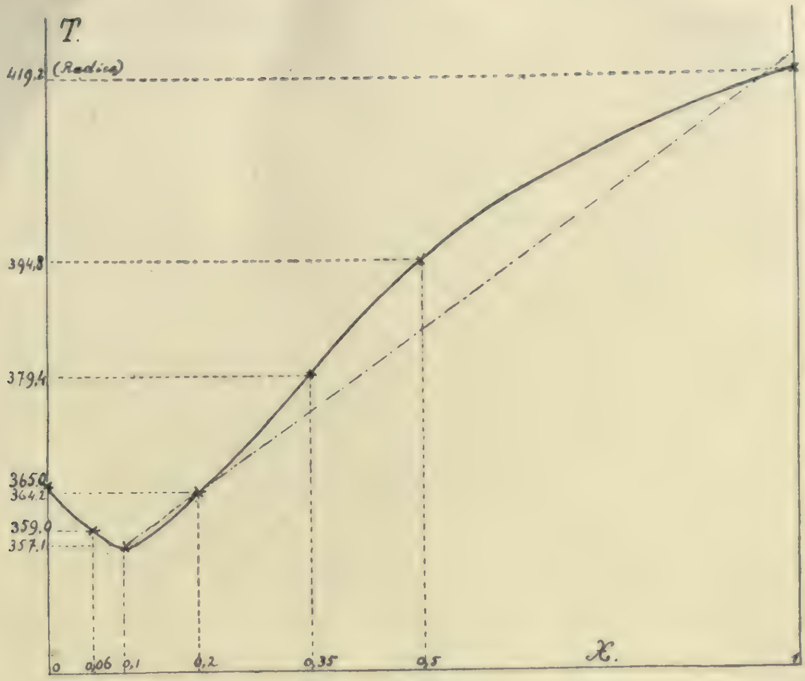
First the T_k of the mixture $x = 0{,}1$ was determined; compared with CAILLETET and COLARDEAU's observations this gave a *decrease* of 8° in the critical temperature. So there was no doubt but a minimum of temperature was present in the plaitpoint-line.

To see whether the decrease would continue, $x = 0{,}2$ was determined: we found ± 364°; the T_k, though rising, was still below the value given by CAILLETET and COLARDEAU for $x = 0$. In order to determine the place of the minimum more accurately, the first component ($x = 0$) and the mixture $x = 0{,}06$ were then examined; finally also $x = 0{,}5$ and $x = 0{,}35$ with a view to the course of the plaitpoint line beyond the minimum.

The observations have been put together in the subjoined table; they have been reduced on a thermometer tested at the Reichsanstalt, which does not show any deviation at 300°, but points one degree too low at 400°.

X	The meniscus disappeared at	The meniscus returned at	The meniscus disappeared for the second time at	The meniscus returned again at
0	365.0	363.9	365.0	364.2
0.06	359.0	358.5	359.0	358.4
0.1	357.0	356.0	357.1	356.0
0.2	364.2	363.0	364.1	363.3
0.35	379.4	378.0	379.3	378.0
0.5	394.8	393.8	394.8	393.9
1	419.2 according to Radice			

Graphically represented we obtain the following Tx-projection of the plaitpoint line:



From this graphical representation follows:

1. that the system water-phenol really possesses a *minimum* plait-point temperature,

2. that it lies in the neighbourhood of $x = 0{,}1$. Now Schreinemakers has found that the mixture $x = 0{,}011$ has maximum pressure at 56°, the mixture $x = 0{,}015$ at 75°, and $x = 0{,}017$ at 90°. These observations deviate from the theory, for the maximum pressure point does not move to the right with higher temperature, but to the left. If, however, we choose one of Schreinemakers' observations, no matter which, then the fact that the minimum plaitpoint temperature lies at an x *larger* than that of the mixtures for which maximum pressure is still possible, is in accordance with the theory.

3. As the extremities of the ordinates belonging to the abscissae $x = 0.1$, $x = 0.2$, and $x = 1$ lie about on a straight line, and as those belonging to $x = 0.35$ and $x = 0{,}5$ are obviously above it, we must conclude to the presence of a *point of inflection* in the Tx projection of the plaitpoint curve. It is doubtful whether we must attach physical significance to this.

In conclusion I have still to mention that in these observations no electro-magnetic stirring-apparatus has been used, which, however, may be applied as soon as a quartz stirrer of sufficiently small diameter is ready.

Amsterdam, *Physical Laboratory.*

Petrography. — "*The mineralogic and chemical composition of some rocks from Central Borneo*". By J. Schmutzer. (Communicated by Prof. A. Wichmann). [1])

(Communicated in the meeting, of October 31, 1908).

Prof. M. Dittrich at Heidelberg analized the following four rocks, collected by Prof. G. A. F. Molengraaff in Central Borneo:

II 710, a glassy amphiboledacite, found as a boulder on a boulder-bank in the Soengei Sĕbilit, ± 3 KM. above Kĕbijau. [2]).

II 599, the glassy amphiboledacite of which consist the rocks, 1.50 m. high, in the Soengei Embahoe, below Nangah Pĕmali; the hand-specimen was struck close to he contact with the adjacent rock (silicifie tuffbreccia). [3])

II 749, biotiteamphiboleandesite with old habitus from the right bank of the Soengei Tĕbaoeng over against Nangah Oeroei. [4]).

I 893, aplitic microgranite from the waterfall, N.W. cliff, Boekit Kĕlam. [5])

I. *Hyalopilitic Amphiboledacite* (Amphibolephyrivitroyellowstonose).

The grey-black, glassy rock shows a rough, conchoidal fracture; only very indistinctly a few white feldspar-phenocrysts, whose diameter does not exceed 1 mm., and very rare, bright glittering, still smaller green amphibole-needles appear forth from the greasy-shining groundmass. Under the miscroscope the *plagioclase* of the first generation (andesine-oligoclase) forms sharp idiomorphic crystals, lying mostly isolated, but sometimes combining into aggregates. Zonal structure is locally finely developed; among the twin-laws the albite-law reigns, the Carlsbad- and pericline-law occur only subordinately. Here and there the feldspar shows a pronounced inclination to forming skeleton crystals, partly in consequence of differences in the velocity of crystallization in not equivalent directions, by which planes (by preference (010)) broaden lamellarly to far beyond the original boundary ribs, partly by a dense accumulation of glass-inclusions with negative crystal-forms, which at bottom is connected with the same phenomenon. These glass-inclusions press the feldspar-substance together into narrow little laths with two main directions and which combine into a very complicated meandrous pattern, while also the crystal-circumference assumes an irregular indented shape. The glass, however, also forms irregular notch-like or claviform inclusions and is neither in colour, nor in the nature of the microlites to be distinguished from the glass of the groundmass.

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[1]) The Dutch communication was entitled "The mineralogic and chemical composition of some rocks from the Müller-Mountains in Central-Borneo". I avail myself of this opportunity to repair a lapsus calami, only the three first rocks described originating from the Müller-Mountains, Mt. Kĕlam not forming part of this range.

[2]) cf. Molengraaff, Geological Explorations in Central Borneo, Leyden 1902, 209, where this rock is named pitchstore.

[3]) The label bears the indication "$^1/_4$ Km. below Nangah Pĕmali", whilst according to Molengraaff's description, op. cit. 267, and the map VIIIb, published by him at the same time, this should rather be about 100 meters. There can be no doubt, however, about the identity of the rock meant by him in his work l.c., with that described here, as the rock builds up the *first* dyke of andesite in the tuffbreccia below Nangah Pĕmali.

[4]) Mt. Loeboek consists of the same rock, ibid. 298 - 295.

[5]) ibid. 127 (Chapt. VI), 188.

The *amphibole* occurs in fresh little columns and crystal-fragments; the corrosion of the crystals by the magma at the effusion has not given rise to the origin of a proper resorption-border, but has confined itself to rounding the crystals and largely accumulating the magnetite-globulites of the groundmass along their periphery. The dichroism moves between darkgrey-green // the *c*-axis and greenish grey-yellow perpendicularly here to; with regard to the axis of elongation an extinction of 15° was measured. Parallel to (100) and (001) we sometimes find a narrow twin-lamella linked between. Besides the good prismatic cleavage a system of rough cracks shows itself perpendicularly to the *c*-axis. Quartz is wanting.

The *groundmass* consists principally of colourless glass in which excellent idiomorphic lathshaped or tabular feldspars, the former often with fine skeleton-forms and exhibiting a fluidal texture, come to the front. Albite-lamellae and feeble zonal structure are general, glass-inclusions much less frequent than in the phenocrysts; on the other hand the crystals contain many microlites of magnetite and bronzite. Those two last minerals take an important place among the secretions of the base. The magnetite, which on the ground of the chemical analysis seems to contain TiO_2, may, according to the size, be brought to two distinctly separated generations. The intratelluric magnetite (average crystaldiameter 15 μ) forms excellent octahedrons, which occur both in the groundmass and in the phenocrysts. In the groundmass the magnetite crystals are found partly isolated, partly in aggregates and then often grown together to dendritic markings. That the on an average 10 × smaller magnetite-crystals and globulites, occurring by the side of those mentioned above, did not crystallize until the effusion-period, is proved by their accumulation at the circumference of the corroded amphibole-substance. The *bronzite* forms a pretty compact tissue of slender needles, which generally show an irregular transverse cracking. From the feldspar-microlites they are distinguished by the strong refraction, from apatite (occurring as inclusion in the plagioclase-phenocrysts) by their behaviour when tested it by means of a $^1/_4\ \lambda$ mica plate in parallel polarized light, from the very few dichroitic, green, sometimes parallel to a (100) twinned hornblende-prisms of the second generation, mixed up with them, by the very light colour, the weak double refraction and the right extinction.

The grounds on which the presence of bronzite, and not of enstatite or hypersthene is assumed, will further be explained. We can conclude the microscopic description by mentioning the occurrence of extremely fine undefinable microlites with a strong double refraction, whose length is only a few $\mu\mu$, the width by estimate no more than 0.1 μ.

The chemical analysis yielded the following values, from which is calculated the norm of the rock according to Cross, Iddings, Pirsson and Washington 1).

	%	Mol. Prop.	ilm.	orth.	alb.	anorth.	cor.	magn.	bronz.	quartz
SiO_2	66.16	1.103	—	126	384	124	—	—	33	436
Al_2O_3	15 39	0.151	—	21	64	62	4	—	—	—
Fe_2O_3	1.25	0.0 8	—	—	—	—	—	8	—	—
FeO	1 72	0 024	6	—	—	—	—	8	10	—
MgO	0 90	0.023	—	—	—	—	—	—	23	—
CaO	3 47	0.062	—	—	—	62	—	—	—	—
Na_2O	3.94	0.064	—	—	64	—	—	—	—	—
K_2O	2.00	0.021	—	21	—	—	—	—	—	—
H_2O 1)	4.94	—	—	—	—	—	—	—	—	—
TiO_2	0.50	0.006	6	—	—	—	—	—	—	—
	100.27									

1) Loss of ignition 5.11 %

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1) Quantitative classification of Igneous Rocks, Chicago, 1903.

From this the following norm may be calculated:

quartz	26.16	$Q = 26.16$	Sal = 89.03
orthoclase	11.68	$F = 62.46$	
albite	33.54		
anorthite	17.24		
corundum	0.41	$C = 0.41$	
bronzite	3.62	$P = 3.62$	Fem = 6.39
magnetite	1.86	$M = 2.77$	
ilmenite	0.91		

so that according to the American system the rock belongs to Class 1 (Persalane); Subclass 1, (Persalone); order 4 (Brittanare); Rank 3 (Coloradase); Subrank 4 (Yellowstonose). The only positive deviation, which the mode shows with respect to the norm, is the presence of amphibole, so that the described rock ought to have the name of Amphibolephyrivitroyellowstonose [1].

The chemical analysis throws some light on the nature of the rhombic pyroxene. The microscopic examination stopped at the observation that the pyroxene was distinguished from the hypersthene by its light colour. The above combination of the oxydes to mineral-molecules now proves that in the pyroxene-molecule MgO predominates strongly with respect to FeO. That the mode of the rock by the appearance of amphibole deviates somewhat from the norm calculated here, does not alter this fact considerably; even if we set aside the circumstance, that the amphibole is quantitatively far inferior to the crystalized rhombic pyroxene. For the fact that in the resorption of the amphibole-phenocrysts only magnetite, no pyroxene as a new

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[1] In spite of the lack of quartz in this rock, it is, on the ground of the high SiO_2 quantity, ranked not under the andesite but under the dacite: the same thing was done with the rock II 599 from the Soengei Embahoe. With the rock-analyses, gathered by Osann, Beiträge zur chemischen Petrographie, II Teil, Stuttgart 1905, the above types are grouped as follows after the SiO_2 quantity (not free from H_2O):

SiO_2 in %	75	74	73	72	71	70	69	68	67	66	65	64	63	62	61	60	59	58	57	56	55	54	53	52	51	50
Nr. of analyses Dacite	1	—	1	—	3	5	4	7	3	4	3	3	2	1	1	—	—	—								
Nr. of analyses Andesite				—	—	—	1	2	1	10	6	10	9	11	20	24	16	13	10	16	12	6	2	3	3	—

From this may be calculated that the SiO_2 quantity with the dacite is fluctuating round a mean of 67.5 %, with the andesite round 59.5 %. Of course these figures have only a very relative value; the rocks II 710 and II 599 however take up places also in the projection-triangle of Osann which fall entirely within the sphere of the dacite- and quartzporphyriteprojections, but only near the border of the sphere of the andesites (glimmer-, hornblende-, hypersthene resp. augiteandesites and porphyrites, cf. Osann, Versuch einer chem. Classification der Eruptivgesteine, Tsch. Min. Petr. Mitt. XX, Heft 5. 6 1900, Taf. IX, X).

secretion shows itself, justifies the supposition that the amphibole must be said to belong to the ferruginous varieties, and from this may be concluded that the ratio of the oxyde-quanta MgO and FeO, which after the crystallization of the amphibole remained available for the formation of rhombic pyroxene, could not be altered very much at the expense of MgO, compared with the ratio which the norm-calculation yields. These different grounds, therefore, tell against hypersthene, and for bronzite or ferruginous enstatite. In accordance with our conclusion, as will appear further on, unmistakable enstatite-(bronzite-)crystals of greater dimensions are found in the glassy dacite II 599 of the Soengei Embahoe, which has a close chemical and mineralogic similarity with this rock. There, too, the glass-base possesses the same characteristic rhombic pyroxene microlites, whose bronzite-nature is made probable by the chemical analysis.

Fe_2O_3 being reduced to FeO, the molecular proportions, calculated on a sum of 100, yield the following values (TiO_2 added to SiO_2):

SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O
75.45	10.27	2.72	1.56	4.22	4.35	1.43

from which follows the formula according to Osann:

	s	A	C	F	a	c	f	n	m	k	Series
I	75.45	5.78	4.49	4.02	8.09	6.28	5.62	7.53	10.00	1.46	*α c*
II	75.45	5.78	4.22	4.29	8.09	5.90	6.00	—	—	—	
III	—	—	—	—	(12.14	9.42	8.43)	—	—	—	
IV	—	—	—	—	(12.14	8.85	9.00)	—	—	—	

These figures require some explanation. As appeared already at the calculation of the norm, there remained after saturation of the alkalis and CaO with Al_2O_3 a not unimportant quantity of sesquioxyde. The analyzed material being absolutely fresh and even microscopically free from every trace of decomposition, there is no possibility of a relative increase of Al_2O_3 by a removal of alkalis and CaO: a consequent distribution of the Al_2O_3-remainder over alkalis and CaO[1] could not be reasonably defended here. Also the dissolution by the andesite-magma of fragments from an adjacent rock rich in aluminium cannot but be highly improbable; both macroscopically and microscopically there is not the least indication for it. For the rest the Al_2O_3-remainder cannot be found in amphiboles or pyroxenes[2] exceedingly rich in Al_2O_3, as appears sufficiently from the microscopic examination; it has on the contrary to be looked for in the glass of the groundmass.

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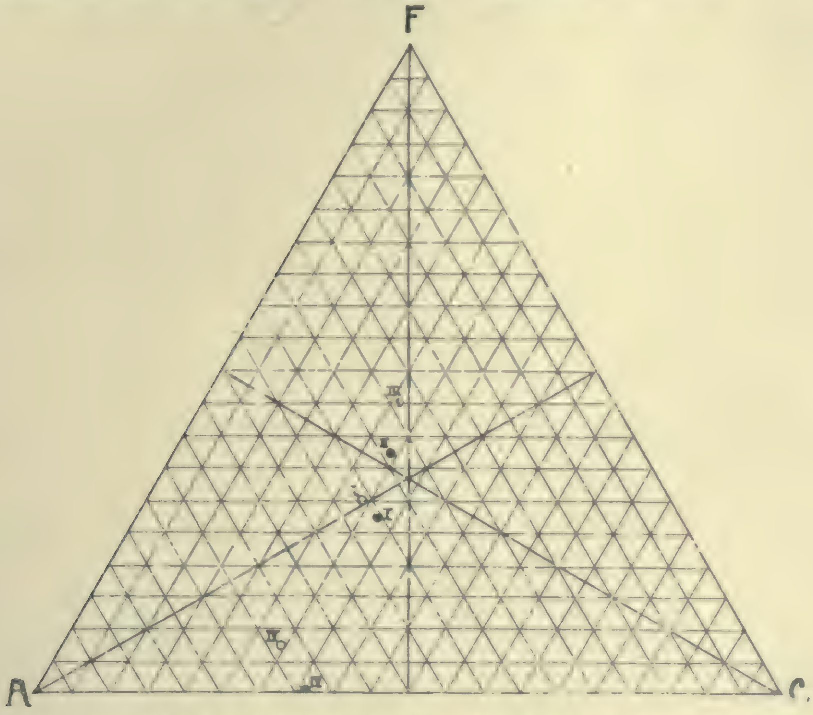
[1] L. Milch, Ueber Spaltungsvorgänge in granitischen Magmen nach Beobachtungen im Granit des Riesengebirges, Festschrift H. Rosenbusch, 1906, 127.

[2] A. Osann, Versuch einer chemischen Classification der Eruptivgesteine, Min Petr. Mitt. XXII, 1903, 337.

In the rare cases, in which after saturation of the alkalis and lime an Al_2O_3-remainder shows itself, Osann substitutes MgO in the atom-group $CaAl_2O_4$ [1]), whilst Becke [2]) neglects the Al_2O_3-rest in the formula and mentions it separately; it amounts here in molecular proportions to 0.27. Accordingly in I the rock-formula is given according to Osann, in II after Becke. In III and IV these double values for a, c and f after Becke have been calculated on a sum of 30 instead of 20 (I and II).

In the following graphic notation I denotes the projection of the rock; the filled circle with the values of a, c, f according to Osann as base, the one not filled with those according to Becke.



II. *Hyalopilitic Amphiboledacite* (Amphibolephyrivitroyellowstonose). From the glassy base of this greasy-shining, blackish grey rock, which shows an inclination to a conchoidal fracture and in one of the hand-specimens a distinct and pretty regular separation into thin, level plates from 1—7 mm. in thickness, already macroscopically small plagioclases with lively microtine-habitus and glittering amphibole-prisms are coming forth. The very fresh, also here mostly idiomorphic, prismatic and tabular *plagioclase*-phenocrysts are often lying together in groups and possess an excellent zonal structure showing itself already in obliquely transmitted ordinary light by parallel strongly luminous stripes and in which acid and basic zones frequently interchange. The same twin-laws are found as in the preceding rock; the albite-lamellae sometimes fit into each other with irregular indentations, in consequence of which through the growing together of several crystals a confused polarization-image arises. The plagioclase of the phenocrysts belongs to somewhat more basic mixtures than in the preceding dacite; the basicity falls to that of basic labrador, but on the other side approaches that of andesine. The crystallization of the basic plagioclase had already ended before that of the amphibole-phenocrysts, but for a time coincided with it; the more acid plagioclase on the other hand often contains amphibole-prisms inclosed. According to the dimensions the plagioclases in this rock may be divided into three groups: *a*) crystals with an average diameter of 1.5 mm., generally strongly laden with colourless and brown glass-inclusions and often entirely filled with these, with the exception of a peripheric zone: *b*) crystals, on an average twice as small and in which the brown glass-inclusions are very rare, the colourless ones on the whole being much less numerous; *c*. still smaller prismatic crystals, which always show a zonal structure and a twinning after the albite- and Carlsbad-law, and which gradually pass into the youngest and smallest skeleton-shaped, mostly fluidally arranged feldspars of the glass-base. Whilst *b* has still to be reckoned among the real phenocrysts, *c* had better be placed in the second generation. As appears, the boundary-line between the crystals of the 1st and 2nd generation can with the feldspars not be drawn exactly, though there is no doubt about the extremes. Higher up we mentioned the appearance of two kinds of glass-inclusions, which also here often assume the form of negative crystals: 1. of almost colourless ones, which seem to have a very light pink tinge and sometimes contain numerous microlites and 2. of brownish grey ones, which are strongly spherolitically devitrified. The nature of this brown glass, also occurring in patches in the colourless glass-base, is not quite obvious. Only it seems to be certain that the brown glass has no genetic relation with the colourless. But then these two sorts of glass must have existed side by side as far back as the intratelluric period, as they occur by the side of each other in the plagioclase and amphibole phenocrysts. Therefore the brown glass probably contains dissolved foreign matter, or, what is perhaps more acceptable, it is a product of intratelluric liquation.

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[1]) Min. Petr. Mitt. XXII, 1903. 337.

[2]) Ibid. 215.

The *amphibole*, which abundantly occurs, forms blunt needles, not exceeding a length of 1 mm.: 𝔠 = green, 𝔟 = greyish green and 𝔞 = greyish yellow, in which 𝔠 > 𝔟 > 𝔞, but 𝔠 and 𝔟 differ only insignificantly. Now and then a zonal structure comes to the front, which is perceptible especially in some sections perpendicular to the axis of elongation. In this case there is seen parallel to the crystal-circumference a zone, showing the colours 𝔞 = blue greyish green or dark greyish green, 𝔟 = brown greyish green, 𝔠 = light greyish green. The idiomorphic crystals have often been so strongly affected by resorption, that the groundmass penetrates into them with deep windings. The resorption-border is formed by an exceedingly dense felt-like tissue of fine microlites, becoming larger here and there, in some places even exceeding the feldspar-laths of the groundmass in size and which can then with certainty be recognised as a rhombic pyroxene. Mixed with them we find magnetite and strongly double-refracting grains, which have probably to be taken for augite. The resorption-border is not everywhere distinctly developed, in some crystals it seems even to be wanting partially. An explanation of this might be given by the supposition that the rock, even after the resorption-period, has been raised with violence, by which movement the components of the resorption-border were in some places swept away from the phenocryst. This conception is positively backed by the observation that the border often passes cloudlike into the groundmass, while the bigger needles pretty generally by transversal cracks are broken into pieces, which have lost their mutual orientation. But besides the components of the first generation show mechanical deformations, which have come about before the solidification of the glass-base and in all probability after the resorption-period. The feldspar shows irregular fissures and rents, along which pieces of broken twin-lamellae have sometimes moved with respect to each other and which are filled with glass of the groundmass as soon as the fragments through a mutual transposition are no longer closely united.

By irregular cracks perpendicular to the axis of elongation, the amphibole too is nearly always broken into fragments, which are often tolerably far carried away from each other; not rarely also opened wide along the cleavage directions. Also here the gaping rents are filled with glass and stress is to be laid upon the fact that this glass is nearly always entirely free from the resorption-products, which show themselves along the original crystal-boundaries. This proves that those rents were opened at an epoch when the resorption-period was all but over, a conclusion which is wholly in accordance with the above fact that the needles themselves, forming the resorption-borders, are frequently broken. This makes the existence of a third phase in the cooling-process of the rock plausible, which affords a striking parallelism with the existing different feldspar-generations described.

To the second generation belong strictly idiomorphic crystals of rhombic pyroxene, somewhat bigger than the described needles out of the resorption-border, but genetically identical with them. They are often parallelly grown together; the planes (100) and (010) are strongly developed and sometimes push away the prismplanes (110) (1$\bar{1}$0) entirely. To the latter a distinct cleavage runs parallel; in some places also a pinacoidal splitting shows itself. They have a light-grey colour and display a slight dichroism. Some excellent sections ⊥*c* yielded in convergent light centrally the locus of an acute positive bisectrix, so that, added to this the right extinction, the *enstatitic* (bronzitic) nature of the mineral is certain.

The *groundmass*, finally, is formed by a glass-base, in which, besides the above feldspars, occur: amphibole-prisms of much smaller dimensions than the proper phenocrysts, which, however, pass into them without a distinct limit of size, and as appears from the dense peripheric microlite-border belong to the first generation; magnetite, just as in the described dacite II 710, present in two generations, and numberless bronzite-needles with the characteristic rough cracking // (001). Apatite occurs as inclusion in the amphibole.

The chemical analysis of the rock yielded:

	%	Mol. Prop.	ilm.	magn.	orth.	alb.	anorth.	diops.	bronz.	quartz
SiO_2	65.72	1.095	—	—	72	408	136	14	42	423
Al_2O_3	15.06	0.148		—	12	68	68	—	—	—
Fe_2O_3	1.35	0.009	—	9	—	—	—	—	—	—
FeO	1.80	0.025	6	9	—	—	—	7	42	—
MgO	1.57	0.039	—	—	—	—	—			—
CaO	4.18	0.075	—	—	—	—	68	7	—	—
Na_2O	4.24	0.068	—	—	—	68	—	—	—	—
K_2O	1.07	0.012	—	—	12	—	—	—	—	—
TiO_2	0.48	0.006	6	—	—	—	—	—	—	—
H_2O −105°	0.09	—	—	—	—	—	—	—	—	—
H_2O + 105°	3.77	—	—	—	—	—	—	—	—	-
	99.93									

From which follows the following norm:

quartz	25.38	Q = 25.38	Sal = 86.58
orthoclase	6.67	F = 61.20	
albite	35.63		
anorthite	18.90		
diopside	1.54	P = 6.03	Fem = 9.03
bronzite	4.49		
ilmenite	0.91	M = 3.00	
magnetite	2.09		

and the rock is placed in Class I (Persalane); Subclass 1 (Persalone); Order 4 (Brittanare); Rank 3 (Coloradase); Subrank 4 (Yellowstonose).

If we take into consideration that the diopside-molecule is crystallized as amphibole, there is a satisfactory agreement to be observed between norm and mode.

If Fe_2O_3 is reduced to FeO, the molecular proportions, calculated on a sum of 100 (TiO_2 added to SiO_2) give the following values:

SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O
74.14	9.97	2.83	2.63	5.05	4.58	0.81

so that the formula according to Osann is:

	s	A	C	F	a	c	f	n	m	k	Series
I	74.14	5.39	4.58	5.93	6.78	5.76	7.46	8.5	9.2	1.56	*av*
II					(10.17	8.64	11.19)				

In I $a + c + f = 20$; in II $a + c + f = 30$.

Both dacites, therefore, show a great chemical similarity, which is also expressed by the graphic notation, fig. 1. The somewhat greater basicity of the second rock, which contains more CaO and MgO, a little less SiO_2, and half the quantity of K_2O, manifests under the microscope by the character of the feldspars and the greater quantity of amphibole.

In order to compare them some analyses have been brought together, which show a great similarity with the two discussed above:

	I	II	III	IV	V	VI	VII
SiO_2	67.34	66.16	65.88	65.72	65.66	65.39	64.81
Al_2O_3	15.96	15.39	15.61	15.06	15.61	15.49	15.73
Fe_2O_3	3.38	1.25	2.42	1.35	2.10	2.80	1.68
FeO	0.80	1.72	2.71	1.80	2.07	1.99	2.91
MgO	0.88	0.90	1.76	1.57	2.46	2.06	2.82
CaO	2.98	3.47	3.70	4.18	3.64	4.48	4.22
Na_2O	4.12	3.94	3.92	4.24	3.65	4.56	3.98
K_2O	1.66	2.00	2.29	1.07	2.03	1.59	1.43
H_2O+	2.20	4.94	1.05	3.77	1.07	0.55	0.62
H_2O-	—	—	—	0.69	—	—	—
CO_2	—	—	sp.	—	—	—	—
TiO_2	0.56	0.50	0.43	0.48	1.37	—	0.08
P_2O_5	—	—	0.13	—	sp.	0.11	0.23
MnO	—	—	0.08	—	—	—	0.08
Sum	99.78	100.27	100.00	99.93	100.27	99.02	100.61

I. Biotitedacite, Kolantziki, Megara, Greece, anal. A. Röhrig, cf. Washington, Journ. Geol. III, 150, 1895 (Yellowstonose).

II. Amphiboledacite, boulder from boulder-bank, Sebilit-river, ±3 KM. above Kĕbijau, anal. M. Dittrich.

III. Granitite, Mazaruni District, Brit. Guyana, anal. J. B. Harrison, cf. Washington, Chem. Anal. of Igneous Rocks, 1903, 191 (Yellowstonose).

IV. Amphiboledacite, first dyke below Nu Pemali, Embahoe-river, anal. M. Dittrich.

V. Dacite, Sepulchre Mountain, Yellowstone nat. Park, anal. J. E. Whitfield, cf. J. P. Iddings, XII Ann. Rep. U. S. Geol. Surv. I, 648, 1891 (Yellowstonose).

VI. Pyroxenedacite (Quartzpyroxeneandesite), Cumbal, Columb. Andes, cf. Küch, N. Jahrb. f. Min. 1886, I.

VII. Biotiteporphyrite, North Mosquito, Col., anal. Hillebrand, cf. Cross, XII^ Monogr. U. S. Geol. Surv., Clarke, U. S. Bull. No. 168, 155. (Yellowstonose).

III. *Biotiteamphiboleandesite* (Biotiteamphibolephyrovitritonalose).

The rock of which Boekit Loeboek is composed, and of which the handspecimen II 749, struck over against Nangah Oeroei on the Soengei Tèbaoeng, represents a sample, belongs to the freshest old andesites of the Western Müller-mountains. After the macroscopic habitus it takes a place quite by itself; a darkgreen groundmass, strongly fading in the more weathered rock, forms the cement between irregularly scattered plagioclases with microtine-habitus, sometimes densely crowded together and reaching a diameter of 6 mm., slender amphibole-crystals (to 8 × 2 mm.) and hexagonal little tables of bronze-coloured biotite (3- 4 mm. diam.). The twinned, often very distinctly zonal *plagioclase* is not really different from the one described above. The very first beginning of decomposition shows itself in a slight development of albite, secondary amphibole and troubling substances along cracks. The plagioclase, for the rest limpid, contains as inclusions primary amphibole, often twinned parallel to (100), magnetite, apatite, and occasional sharp prisms of zircone, whilst peripherically sometimes augite-grains are inclosed, which are characteristic of the resorption-borders of the amphibole-phenocrysts, and from this appears that the crystallization of the plagioclase did not come to an end until during or after the eruption.

The *amphibole* forms prismatic individuals, which are strongly corroded by the magma and surrounded by a broad, loose border of chloritizing amphibole-scales, pyroxene-, magnetite- and titanite-grains, mixed with the usual groundmass-components. Slender prisms are sometimes, to within a narow, notched lath, entirely changed into these products. The extinction with respect to the *c*-axis reaches a value of 20°; the pleochroism varies between dead brownish green and light brownish green; the usual twins parallel to (100) occur. As for inclusions the amphibole contains basic plagioclase, magnetite and cloudlike accumulations of extremely fine, parallel microlites, which probably, quite like a part of the magnetite-globulites, owe their individualisation to a chemical dissociation of the amphibole substance. The examination of the *biotite* yields no particular points of view. The acid *groundmass* consists of probably primary grains of quartz with wavy extinction containing colourless limpid glass-inclusions, sanidine and acid, short prismatic and zonal, but also slender lath-shaped plagioclase with polysynthetic twinning after the albite-law; these minerals are cemented by a small amount of colourless glass, strongly troubled by globulites. Here and there some grains of almost colourless augite, sometimes twinned and strongly laden with glass, are found, which as appears from their occurrence near the resorption-zones of the amphibole-phenocrysts, even there, where they assume more considerable dimensions (to 0.1 mm.), must be considered as resorption-products. The glass of the groundmass contains magnetite in octrahedrons, grains and prisms of apatite and of zircone, and is everywhere pushed away by fibres and little scales of a green chloritic product, strongly accumulating round the amphibole-phenocrysts and having formed principally at the cost of the secondary amphibole secreted in the resorption.

The analysis of the freshest material gave the following results:

	°/0	Mol. Prop.	ilm.	magn.	ham.	orth.	alb.	anorth.	diops.	enstat.	quartz
SiO_2	62.70	1.045	—	—	—	114	396	152	22	52	309
Al_2O_3	16.37	0.161	—	—	—	19	66	76	—	—	—
F_2O_3	2.81	0.018	—	14	4	—	—	—	—	—	—
FeO	1.62	0.022	8	14	—	—	—	—	—	—	—
MgO	2.50	0 063	—	—		—	—	—	11	52	—
CaO	4.84	0.087	—	—	—	—	—	76	11	—	—
Na_2O	4.05	0.066	—	—	—	—	66	—	—	—	—
K_2O	1.83	0.019	—	—	—	19	—	—	—	—	—
$H_2O - 105°$ $HO + 105°$	0.87 1.79	—	—	—	—	—	—	—	—	—	—
TiO_2	0.64	0.008	8	—	—	—	—	—	—	—	—
	100 02										

from which follows the composition:

Quartz	18.54	Q = 18.54	Sal = 84.81
orthoclase	10.56	F = 66.27	
albite	34.58		
anorthite	21.13		
diopside	2.38	P = 7.58	Fem = 12.69
enstatite	5.20		
ilmenite	1.22	M = 5.11	
magnetite	3.25		
haematite	0.64		

The rock therefore belongs to Class II (Dosalane); Subclass I (Dosalone); Order 4 (Austrare); Rank 3 (Tonalase); Subrank 4 (Tonalose). The greater basicity with respect to the above mentioned rocks shows itself chemically in the decrease of the SiO_2, the increase of the MgO and the CaO quantity. The mode deviates rather considerably from the norm by the presence of biotite and amphibole, which minerals have to be considered as the bearers of the MgO, which is put here under the enstatite-molecule. A portion of the MgO, however, also occurs in the augite and the amphibole of the resorption-border and in the chlorite.

The molecular proportions calculated on a sum of 100 — Fe_2O_3 reduced to FeO — yield:

SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2
69.34	10.68	3.85	4.18	5.77	4.38	1.26	0.53

Formula according to Osann:

s	A	C	F	a	c	f	n	m	k	Series
69.87	5.64	5.05	8.75	5.8	5.2	9	7.7	9.2	1.33	*a v*
				(8.7)	(7.8)	(13.5)				

In the graphic notation it is the basic character which, by the side of the close similarity between the two preceding dacites, is distinctly expressed. To make a comparison we give here the analyses of some chemically closely allied rocks:

	I	II	III	IV	V	VI
SiO_2	62.78	62.70	62.27	62.09	62.09	61.22
Al_2O_3	17.16	16.37	16.92	17.03	16.69	16.14
Fe_2O_3	1.96	2.81	2.40	2.38	1.45	3.01
FeO	2.31	1.62	2.59	2.69	3.76	2.58
MgO	2.32	2.50	2.87	3.08	1.93	4.21
CaO	4.84	4.84	4.78	5.65	6.08	5.46
Na_2O	4.11	4.05	4.72	4.10	3.36	4.48
K_2O	2.15	1.83	1.47	1.67	1.84	1.87
H_2O+	0.88	1.79	1.22	0.13	1.47	0.40
H_2O-	0.24	0.87	—	0.04	0.19	0.04
TiO_2	0.56	0.64	0.16	0.65	0.32	0.61
P_2O_5	0.15	—	sp.	0.19	0.39	0.25
MnO	0.06	—	—	sp.	sp.	sp.
BaO	0.04	—	—	0.07	0.10	—
Som	99.58	100.02	99.47	99.84	99.77	100.36

I Yentnite, Yentna River, Alaska; anal. H. N. Stokes, cf. J. E. Spurr, Am. Journ. Sci. X, 310, 1900 (Tonalose; included in the sum: S = 0.02, and traces of Cl, SrO, Li_2O).

II Biotiteamphiboleandesite, right bank of Tĕbaoeng-river, opposite N^a. Oeroei, Central-Borneo, anal. M. Dittrich. (Tonalose).

III Andesite, Punta della Civitate, Capraja-isl., Italy, anal. A. Röhrig, cf. H. Emmons, Quart. Journ. Geol. Soc. XLIX. 142, 1893 (Cl = 0.07 ; Tonalose).

IV Hypersteneaugiteandesite, Palisades, Crater Lake, Oregon, anal. H. N. Stokes, cf. H. B. Patton, Bull. U. S. Geol. Surv. 168, 223, 1900 (SrO = 0.07 ; Tonalose).

V Hornblendeporphyrite, Nevada City, Calif., anal. H. N. Stokes, cf. W. Lindgren XVII Ann. Rep. U. S. Geol. Surv. II, 59; 1896 (SO_3 = 0.10, Tonalose).

VI Pyroxenemicadiorite, Electric Peak, Yellowstone Nat. Park.; anal. W. H. Melville, cf. J. P. Iddings, XII Ann. Rep. U. S. Geol. Surv. I, 627, 1891 (NiO = 0.09, Tonalose).

IV. *Aplitic Microgranite* (normat. Graniphyrilassenose).

The rough, pure white, powdery, very fine-grained rock often contains holes, in which appear mica-rosettes and serpentinous products, which also in microscopic aggregates lie scattered through the whole rock and by this betray a certain porosity.

The proper rock-components are mostly rather fresh and in keeping with this the appearance of the secondary products — among which the muscovite takes a foremost place — seems with great probability to have to be attributed to pneumatolytic processes, not to atmospheric weathering. The structure is holocrystalline porphyric, but as such it is only to be recognized microscopically. The very few phenocrysts (average diam. 0.3 mm.) consist of *albite*; they show a little developed idiomorphy, are seldom twinned after the albite-law, but often occur irregularly grown together into groups of 2—3 individuals. A beginning of decomposition shows itself in the appearance of opaque globulites, principally arranged parallel to the cleavage-directions. Quartz and orthoclase-phenocrysts are entirely wanting. The holocrystalline *groundmass* consists of lathshaped, seldom tabular, strongly undulous, and always after the albite-law twinned, irregularly diverging, now and then parallelly arranged acid *plagioclases*, cemented by grains of *quartz* with sometimes tolerably pronounced idiomorphy, then, however, always peripherically cut asunder fringelike by feldspar, mostly, however, without indication of crystallographic boundaries, and further by somewhat orthoclase. The feldspar shows only a very slight beginning of decomposition ; on the other hand, especially scales of secondary colourless mica, beside them serpentinous products and a few irregular crystals of secondary amphibole, together with a here and there condensing globulitic troubling, probably caused by limonite, are often met with in the groundmass. Primary bisilicates, therefore, seem to be entirely wanting in the rock ; the plagioclastic character of the feldspar marks the rock as a basic aplitic facies of microgranite, rich in Na_2O.

The chemical analysis yielded :

	%	Mol. Prop.	magn.	orth	alb.	anorth	cor.	hyp.	quartz
SiO_2	72 44	1.207	—	132	138	88	—	7	542
Al_2O_3	16.51	0 162	—	22	73	44	23	—	--
Fe_2O_3	0.24	0.001	1	—	—	—	—	—	—
FeO	0 52	0.007	1	—	—	—	—	6	—
MgO	0.05	0.001	—	—	—	—	—	1	—
CaO	2 47	0.044	—	—	—	44	—	—	—
Na_2O	4.54	0.073	—	—	73	—	—	—	—
K_2O	2.13	0.022	—	22	—	—	—	—	—
TiO_2	sp.	—	—	—	—	—	—	—	—
$H_2O-105°$ $H_2O+105°$	0.13 1.13	—	—	—	—	—	—	—	—
	100.16								

From which follows the following norm :

quartz	32.52	Q = 32.52	
orthoclase	12.23		
albite	38.25	F = 62.71	Sal = 97.58
anorthite	12.23		
corundum	2.35	C = 2.35	
hypersthene	0.89	P	Fem = 1.12
magnetite	0.23	M	

If we suppose the rock to be fresh, it takes a place in class I (Persalane) ; Subclass I (Persalone) ; Order 4 (Brittanare), Rank 2 (Toscanase) ; Subrank 4 (Lassenose). The question, whether it can be placed in the chemical system must be considered however in connection with the discussed decomposition of the rock. As follows from the microscopic description, the considerable remainder of Al_2O_3 after saturation of K_2O, Na_2O and CaO in the feldsparmolecules must at least for the greater part be attributed to the appearance of muscovite. If we take for muscovite the formula $KH_2Al_3(SiO_4)_3$ [1]), the Al_2O_3-remainder disappears with the presence of 5.84°/₀ orthoclase by the side of 9.15°/₀ muscovite. This last value, however, is exaggeratedly high. If however, in accordance with a microscopic estimate, a quantity of about 3°/₀ muscovite is assumed, and the remainder of the Al_2O_3 is equally divided over K_2O, Na_2O and CaO, in the supposition that these oxydes in the same measure have been removed by solutions, the following composition of the rock is obtained :

quartz	28.32	Q = 28.32	Sal = 95.60
orthoclase	12.79	F = 67.28	
albite	40.87		
anorthite	13.62		
muscovite	3.00		
hypersthene	0.89	Fem = 1.12	
magnetite	0.23		
water	1.11		
Sum	100.83		

Now, if we leave muscovite, as of apparently secondary origin, out of consideration, still then the rock takes the same place in the chemical system :

$$\frac{\text{Sal}}{\text{Fem}} = \frac{95.60}{1.12} > \frac{7}{1}\text{, Persalane}$$

$$\frac{Q}{F} = \frac{28.32}{67.28} < \frac{3}{5} \text{ and } > \frac{1}{7}\text{, Brittanare}$$

$$\frac{K_2O + Na_2O\,^{2})}{CaO} = \frac{23 + 78}{49} = \frac{101}{49} > \frac{5}{3} \text{ and } < \frac{7}{1}\text{, Toscanase}$$

$$\frac{K_2O}{Na_2O} = \frac{23}{78} < \frac{3}{5} \text{ and } > \frac{1}{7}\text{, Lassenose.}$$

Against the name of lassenose can no doubt no serious objections be raised.

Instead of hypersthene the rock contains amphibole and serpentine, the first of which minerals being very rare, whilst the last mentioned is principally confined to the holes, taking as appears from the low MgO-quantity, no important place in the analyzed rocksample.

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[1]) Rosenbusch, Mikrosk. Physiogr. I, 2. p. 262. 1905.

[2]) To each of the K_2O, Na_2O and CaO-molekules 5 has been added, of which 4 K_2O molekules however, go to the muscovite, which is left out of consideration here.

The molecular proportions yield, Fe_2O_3 being reduced to FeO and the whole being calculated on a sum of 100:

SiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O
79.46	10.66	0.66	0.07	2.90	4.81	1.45

the formula according to OSANN:

	s	A	C	F	a	c	f	n	m	k	series
(OSANN)	79.46	6.26	3.63	—	12.66	7.34	—	7.7	—	1.73	*α*
(BECKE)	79.46	6.26	2.90	0.73	12.66	5.86	1.48		(10.0)		

Here we have the rare case that

$$Al_2O_3 > K_2O + Na_2O + CaO + (Mg, Fe)\,O.$$

If, like OSANN, we add MgO and FeO in the molecule $(MgFe)\,Al_2O_4$ to C, there remains a rest of 0.77 Al_2O_3; if however like BECKE we neglect the Al_2O_3 remainder above $(K, Na)_2\,O + CaO$, equal to 1.50, then $C = 2.90$ and $F = 0.73$. The calculation of $a + c + f = 30$ yields:

	a	c	f
(OSANN)	18.99	11.01	—
(BECKE)	18.99	8.79	2.22

In the graphic notation IV denotes the place of the rock; the filled circle the values after OSANN, the not-filled circle the one after BECKE.

Botany. — "*Some systematic and phytogeographical notes on the Javanese Casuarinaceae, especially of the State Herbaria at Leiden and at Utrecht.*" (Contribution to the knowledge of the Flora of Java. N°. III).[1] By Dr. S. H. KOORDERS.

§ 1. Casuarina equisetifolia, Forst.

§§ 1. Geographical distribution outside Java: according to HOOK, Flora Br. Ind. V. 598: in British India on the East side of the Gulf of Bengal, South of Chittagong, in the Malay Archipelago, in Polynesia and in Australia. In the State Herbarium at Leiden I saw, however, also specimens from Madagascar, Mauritius, Bourbon and Senegambia, although it did not appear with certainty from the herbariumlabels, that they referred to uncultivated plants. In Herb. Leiden the species is also represented by specimens from

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[1] Continued from Transactions (Verhandelingen) Roy. Acad. Sciences Amsterdam Second Section Vol. XIV. (1908). N^c. 4.

Hawai and from Australia: in this case one of two specimens (from Sieber) which appear to me to be quite similar, has been determined by Miquel as *C. equisetifolia* Forst. and the other as *C. leptoclada* Miq. In Diels [Die Planzenwelt von West-Australiën südlich des Wendekreises (1906)] the occurrence of some other species of *Casuarina* is mentioned, but not of *C. equisetifolia*. Prof. Dr. L. Diels was so kind as to supply me with the following information on this point: "Casuarina equistifolia kommt in West-Australiën sicher nicht vor. Ob er in Ost-Australiën wächst habe ich persönlich nicht festgestellt, da ich mich dort nur kürzere Zeit aufhielt. Das von Ihnen erwähnte Exemplar, leg. Sieber, stammt aus der Gegend von Sydney, denn dort hat Sieber gesammelt." (Diels msc. 21. IV. 1908). From the Malay Archipelago outside Java I saw *C. equisetifolia* represented in the Herbaria at Leiden and at Utrecht from the following places: Sumatra (leg. Korthals; Teijsmann & de Vriese). Timor (Forbes n. 3746), Moluccas (Reinw.), the North of Dutch New-Guinea (Expedition of Wichmann, determ. Valeton). The examples from Sumatra, collected by Korthals, generally have 8 teeth, as Miquel already noted for these specimens. In N. E. Celebes the species is not found wild: there I only found *C. Rumphiana* Miq. 1).

§§ 2. Geographical distribution and oecological conditions in Java: I have never found *C. equisetifolia* growing wild except in Western-Java in the S.W. of the residency Banten in the division Tjaringin near the village of Tjemara, and there only on a sandy sea-shore, on a small peninsula (= oedjoeng, malay) at sea-level, growing socially.

This may serve as a correction of the statement in Koord. and Valeton "Boomsoorten Java" X (1904) p. 273 (line 12 from top): "*Tjemara (Banten) altit. 200 M. supra mare.*"

Junghuhn says in his Java. I. 2nd edit. (1853) 272: "Were we concerned in dealing with Sumatra, we should have to mention among the trees which grow in groups in the shore forests the Tjemara laoet: *Casuarina equisetifolia* Forst (*muricata* Roxb); nowhere, however, have I found this beach-Casuarina, although natives have assured me, that it is found in some places on the North coast of Krawang" (Junghuhn l. c.). It appears, however, that probably Junghuhn afterwards succeeded in finding this species wild in Java, namely on the Lawoe, although I have not been able to find anything

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1) Koorders, S. H., Eerste Overzicht d. Flora N. O. Celebes (1898) 616; cf. Koorders and Valeton Bijdrage Booms. Java X. (1904) 172 (Mededeelingen Lands Plantent. n°. 19 en 68).

in any publication about this geographically interesting discovery. My surmise is founded on a specimen labelled by JUNGHUHN himself as follows: *Casuarina equisetifolia, E monte Lawu ubi sponte crescit*". This specimen must indeed be regarded as *C. equisetifolia* FORST. according to an autograph determination-label of MIQUEL. I found this specimen in the Leiden Herbarium, registered as H. L. B. n. 10 (899—173) and can confirm the accuracy of the determination of JUNGHUHN and of MIQUEL, for I found on the young branches of JUNGHUHN's specimen, which already bore fruit, that of 14 leafwhorls which I examined, 13 had 7 vaginal teeth and 1 only 6 teeth; the fruit had 12 longitudinal rows. There can therefore be no doubt that this specimen of JUNGHUHN from the Lawoe mountains is completely conspecific with the beach-Casuarina (*C. equisetifolia* FORST.), the more so, since also all other characteristics, e.g. the deeply grooved internodes, $^1/_2$—$^3/_4$ cm. long and $^1/_2$ mm. thick, agree completely with this species. This is the first observed case, so interesting phytogeographically, of the beach Casuarina (*C. equisetifolia*) growing wild in the mountains of Java. The height of this station above sea level is not indicated by JUNGHUHN on the label quoted above. The other Javanese specimens of the State Herb at Leiden and at Utrecht, found by me, are: "Java, on the beach near Batavia and Anjol (leg. JUNGH.); Java (KORTH.; REINW.; TEIJSM.). In the Herbarium at Buitenzorg there are according to KOORD. and VALETON [Bijdr. Booms. Java X (1904) 271] some specimens from the Rahoen-Idjen mountains in Eastern Java, which mostly have 8 vaginal teeth. It appears to me, that we are quite as justified in placing these specimens from the Idjen-plateau under *C. equisetifolia*, as MIQUEL (see above) in the case of the generally 8-toothed beach-Casuarina of the West coast of Sumatra, and KOORDERS and VALETON (l. c. 271) in the case of the beach-Casuarina of S.W. Banten in Western Java, which generally has 7—8 teeth. If the specific limits between *C. montana* and *C. equisetifolia* be drawn as indicated, the distribution of *C. equisetifolia* in Java is as follows: Western Java: in the S.W. of the residency Banten, at sea-level, on a sandy sea-shore on a narrow peninsula (= oedjoeng), at the edge of the surf, growing socially (Herb. Kds in Mus. Bot. Hort. Bogor.). Central Java on the Lawoe growing wild, together with *C. montana* (Herb. JUNGHUHN in Leiden). Eastern Java: in the Rahoen-Idjen mountains, also growing wild with *C. montana* (Herb. Kds in Mus. Hort. Bogor.). Oecological conditions: Limited to soils, which always have little water or which are physiologically dry (containing much salt). Completely wanting on fertile soils, probably because it is crowded out by other species. Although preferably growing wild on sandy sea-shores, and nearly always forming homogeneous woods, it is always wanting in the Javanese Mangrove forests. The tree resists direct sunlight very well, but deep shade very badly. On calcareous soils and in the Javanese Teak-forests it has not yet been observed wild. The species is also completely absent from the mixed, shady, evergreen forests of Java. Evidently it can only maintain itself in the struggle with other species in the above-named unfavourable localities.

§ 2. **Casuarina equisetifolia Forst. var. longiflora,** Miq.! Flora Regensburg. (1865) p. 17; Miq.! in DC. Prodr. XVI. 2 (1868) 339; Boerlage! Handleid. Flora N. I. III. 1. (1900) 404; Koord. and Valeton Bijdr. Booms. Java X. (1904) 272.

For this variety Miquel l. c. gave i. a. the diagnosis: "amentis masculis elongatis glabris; . . . vaginis 7-dentatis" and as locality "Java" (Blume!) without further detail. From the authentic material found by me in the State Herbaria at Leiden and at Utrecht, the following results. The number of vaginal teeth is sometimes 7, as indicated by Miquel l.c. but is often also 6, and sometimes also 8. The male catkins are characterized by the complete absence of hairs, and by their sometimes attaining the exeptionally great length of 40—50 millimetres. On the authentic label the locality is only indicated in Blume's handwriting as: "in Javae oriental. montibus".

A specimen found by me without further indications in the Herbarium at Leiden, which had been sent in 1867 by Teysmann to Hasskarl, and, according to a note added by Hasskarl, was derived from a specimen standing in the Hortus Bogor. [in Herb. Lugd. Bat. sub n. 48 (899/173)], differs so little from the above named authentic specimen, that I suspect the authentic of *C. equisetifolia* Forst. var. *longiflora* Miq. to be also derived from a cultivated specimen in the Buitenzorg Gardens. Both specimens greatly resemble *C. equisetifolia* Forst., but on account of the completely glabrous male catkins they are distinctly different from the type. The number of vaginal teeth in Teysmann's specimen is 7—8, and as in the authentic specimen 6—8.

I further found that not a single of the numerous other Javanese specimens of *Casuarina* in the herbaria at Leiden and at Utrecht, refer to this variety. I have never found the variety wild in Java.

To sum up, I consider it probable, that in this case of *Casuarina equisetifolia* var. *longiflora* Miq. an error of Blume's is the cause of the reputed indigenous occurrence of this plant in Java, an error similar in kind to that which was formerly demonstrated [1]) in the case of another tree cultivated in Hortus of Buitenzorg; it appears, that this variety must be deleted from the flora of Java.

§ 3. **Casuarina montana,** Jungh.! ex Miq. Fl. Ind. Bat. I. 1. (1855) 875 (cum descript.); Jungh.! Java I. ed. 2. (1853) 551—554, 631—639, 663; *C. montana*, Leschen. ex Miq.! in Zoll. Verzeichn. (1854) 86 (nomen tantum); *C. montana*, Miq.! in *A. DC.* Prodr. XVI. 2. (1868) 335; Miq. Illustr. Arch. Ind. (1871) 9. tab. 7. f. 1 et 2; Koord. et Val. Bijdr. Booms. Java X. (1904). 273!; *C. Junghuhniana*, Miq! Plantae Junghuhnianae I. (1854) 7; Miq.! Fl. Ind. Bat. I. 1. (1855) 874; Jungh.! l.c. (1853) 551.

It is evident from the above bibliography, that according to the latest rules of nomenclature this species should not be named *C. montana* Miq., as in Koord. and Val. l.c., nor *C. montana* Leschen., as in the Index Kewensis, but *C. montana* Jungh.

§§ 1. Geographical distribution outside Java: Bangka (Teijsmann n. 7650); Timor (Zipp.; Teijsm.; Forbes n. 3512); Molucc. (Reinw. n. 1504). — On the authentic specimen of Zippel (in H. L. B.) I found on young branches of flowering shoots 10—11 vaginal teeth and generally 11 teeth; internodes 1—$1^1/_3$ mm. thick and about 1 cm. long.

Two fruiting specimens from Timor, named by Miquel himself as *C. montana* have 11—12 teeth, like the var. *validior* Miq., but with thin internodes, corresponding to the var. *tenuior* Miq. — The fruiting specimen of Reinwardt from the Moluccas (without further indication of locality) had ten vaginal teeth throughout and corresponds, also as regards the diameter of the internodes, to the var. *tenuior*. — The fruiting specimen from Bangka bears in Scheffer's handwriting the manuscript name *C. equisetifolia* Forst. var. *bancana*; it has consistently 9 vaginal teeth, fruit cones with about 18 longitudinal rows, cylindrical internodes, $^1/_2$—$^3/_4$ mm. thick about 1 cm. long, and not deeply grooved. This specimen from Bangka cannot in my opinion be separated from some specimens of the Javanese *C. montana* var. *tenuior* Miq. — *C. montana* var. *validior* Miq. I did not find represented in the Herbaria at Leiden and at Utrecht from regions outside Java.

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[1]) Compare the distribution of *Quercus Pinanga* Bl. in Koord and Valeton. Bijdr. Booms. Java X (in Meded. Lands Plant. LXVIII 1904) p 65 and in Koord. Contribution No. 1 to the knowledge of the Flora of Java in Proc. Roy. Acad Sciences. Amsterdam 28 March 1908 p. 772.

§§ 2. Distribution in Java. The var. *validior* Miq. I found represented in the Herb. at Leiden and Utrecht by the following specimens: 1) collected by Junghuhn according to his autograph note on the top of mount Kawi [the second label "Oengaran" which evidently was attached to the specimen at a later date, independently of Junghuhn, cannot, in my opinion, refer to this authentic specimen, for on mount Oengaran not a single *Casuarina* occurs wild]; 2) specimens from Java (without further indications (from Teysm. & De Vriese and 3) a fruiting specimen from Java with the remark "Alpes orientales" (leg. Waitz). In Herb. Kds the var. *validior* Miq. is only represented by specimens from Mt. Wilis at 2000 m. altitude and from Mt. Ardjoeno at 2100—2400 metres; only the specimens from mount Ardjoeno are characteristic, for the determination of the variety of the specimens from the Wilis is not quite certain. The authentic specimen of Junghuhn from the top of Mt. Kawi (in Herb. Leiden) I found to have internodes of about 1 cm. long with a diameter of 1—1½ mm., and with 10—11 vaginal teeth. The specimen of Waitz generally had 11 vaginal teeth. The Javanese examples of var. *tenuior* Miq. are only represented in the Herbaria at Leiden and Utrecht by a few specimens of Korthals and of Teysm. & De Vriese from "Java" (without further indications) and by a fruiting specimen (Kds. 37348 β Comm. ex museo bot. Hort. Bogor.), collected fruiting in October 1899 in Eastern Java on Mt. Tengger near Ngadisari at 2000 metres altitude. In the extensive alpine Casuarina-forests of Mt. Rahoen-Idjen in Eastern Java I found only var. *tenuior* Miq. whereas var. *validior* appeared to be wholly wanting there. On Mt. Wilis in Central Java I found in the Casuarina-forests almost exclusively var. *tenuior* Miq., but there nevertheless a small number of individuals belonging to var. *validior* Miq. were also found; the form with internodes $1^{1}/_{2}$ mm. thick, which is characteristic for the top of Mt. Kawi, could not be found on Mt. Wilis. The youngest twigs of var. *validior* Miq., occurring on the latter mountain, where at most 1 mm. in diameter. Junghuhn mentions (Java. I (1853) p. 551), that *C. montana* first occurs on the Lawoe and thence eastwards covers the tops of all the mountains, which rise above 1500 metres, but is wholly absent from Western Java. As a result of my own observations I can confirm this statement. Concerning the vertical distribution of *C. montana* var. *tenuior* Miq. in the Wilis mountains on the Darawati summit in the residency Madioen. I append here, what I published on this subject in 1894 in a Dutch article "On the composition of some forests in the residency of Madioen" (in Tijdschr. v. Nijverh. en Landb. in N. Indië XLVIII (1894) part 4 p. 18—22 namely in the chapter "[To the top of the Wilis. Ascent of the Darawati]: "At 7^{40} = 1670 m. altitude the mixed shady forest of high trees suddenly ceases, at least on the ridge, for in the valleys it continues further northwards and we arrive at a small alang-alang field with scattered young trees of *Albizzia montana* Benth. and immediately after this we see the first specimens of *C. montana* Jungh".

From this point, at about 1700 m. altitude, the ridge, which leads to the summit of the Darawati, is completely covered with this tree alone. On the slopes (and even almost right up to the ridge) other trees grow, up to an altitude of 2000 meters. Not until this altitude is reached, do *Casuarina's* occur in the valleys." [Koord. l. c. (1894) p. 19—20 of the reprint]. From this it results, that *Casuarina montana* var. *tenuior* is not found on mount Wilis below 1650 m. altitude, but that it occurs from there upwards to the highest top, at 2550 m. altitude. These data, and those about to be given, should be substituted for the figures of vertical distribution, published in Koord. and Valeton Bijdr. Boomsoorten Java X (1904) p. 274.

I may further add, that also on journeys undertaken by me after the above-named year (1894) in the residency of Madioen, I *nowhere* found *C. montana* growing wild below 1650 m. altitude. It is indeed interesting, that this species at once forms forests, almost from the spot, where it first appears, and above 2000 m. not only covers the higher ridges, but also the valleys, almost to the exclusion of other trees. In the teakforests of Madioen, as in other parts of Java, I have only found *C. montana* and *C. equisetifolia* here and there cultivated (e. g. near pasanggrahans, along road-sides, etc.) but never growing wild. On the Idjen-plateau in the residency of Besoeki *C. montana* var. *tenuior* descends somewhat below the vertical limit of 1500 m. At this lower limit of distribution *C. montana* var. *tenuior* grows only on the dry mountain ridge, whereas it is crowded out from the ravines and moist places by other trees. On Mt. Tengger in 1899 I made the following note on the var. *tenuior*: A large tree attaining 35 m. with a trunk of $1\frac{1}{2}$ m. in diameter; on steep rocks at 2000 m. altitude often only 20 m. high with a trunk 30 cm. diam. On Mt. Tengger forming forests, especially between 2200—

2800 m., but on the ridges of the N.E. side of the range descending to 1600 m. altitude.

Although adult trees cannot well stand deep shade, this does not apply to very young individuals. This is evident from the following note made by me in 1891 [1]): Small trees of *Albizzia moluccana* BENTH., which had shot up after a forest fire in August 1891 on mount Wilis (in Java) at an altitude of about 1800 m., had were $1^{1}/_{2}$—2 m. high, when I ascended the mountain on October 15th 1891, and there so crowded together, that these naturally grown Albizzia-woods resembled nursery beds. Under these, in fairly deep shade, I found numerous seedlings of *Casuarina montana*, growing wild and about 0.2 m. high.

The distribution and the oecological conditions of *C. montana* var. *tenuior* may be characterized as follows: Extraordinarily great power of resisting drought, strong winds and the strong direct sunlight of the alpine region, and, but only in earliest youth (*not* later) power of resisting shade. Very common in Central Java at 1650—3000 m. and in the eastern part of Eastern Java at about 1400—3000 m. altitude, but wild growing quite unknown west of mount Lawoe, indigenous not known either from the mount Oengaran [in contradiction to the inaccurate statement of MIQUEL in his Flora Ind. Bat. I. 1. p. 875].

§ 4. Means of distribution of Casuarina equisetifolia and C. montana.

Both species appear to be well adapted for distribution by wind, and in spite of the negative results of GUPPY's floating experiments, they seem also adapted for distribution by ocean currents.

In the winged fruit of Javanese specimens, examined by me, I observed the following dimensions. *C. equisetifolia* FORST.: fruits $1^{1}/_{2}$ — 2 mm. long and 1 — $1^{1}/_{2}$ mm. broad compressed laterally, with a very thin, obovate wing, 5 mm. long and 3 mm. broad. In *C. montana* var. *tenuior* MIQ.: fruits $1^{1}/_{2}$ — $1^{3}/_{4}$ × 1 — $1^{1}/_{2}$ mm., strongly compressed laterally, with very thin ovate wing, 2—$2^{1}/_{4}$ mm. long and $1^{1}/_{2}$ — $1^{3}/_{4}$ mm. broad.

In his well-known experiments, on the floating of fruits and seeds GUPPY found, that the fruit cones of *Casuarina equisetifolia* FORST. remain floating on a $3^{1}/_{2}$ percent solution of common salt for 1—2 days at the most. This period is not, however, sufficient to account for the known, wide over-sea distribution of this species. On repeating the experiment of GUPPY, I could only confirm the shortness of the floating period for separate fruit cones. I found, however, that the floating period on a similar salt solution is so much greater for fruitlets, which have been liberated from the cone (e. g. by dessication), that the wide distribution now becomes quite intelligible, if one but supposes, that the germinative power is not damaged by a sojourn of one month in sea-water. On this point, however, no experiments have as yet, to my knowledge been made. Meanwhile I feel justified in deducing from the anatomical structure of the fruitlets, that the embryo is most probably sufficiently protected against the entry of sea-water. In some flotation experiments I found that after one month 100°/₀ of the fruitlets of *C. equisetifolia* Forst., and upwards of 75°/₀ of those of *C. montana* Jungh. var. *tenuior* Miq. remained floating.

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[1]) Compare KOORD. and VALETON Bijdr. Booms. Java II. (1895) 294.

Besides by anemophilous and hydrophilous distribution, *C. equisetifolia* and *C. montana* can spread by rootsuckers. The latter are however rarely found in these species further than 10 m. from the main trunk. Should the main trunk die off (for instance in consequence of a fire) one can often observe, e. g. with *C. montana*, that a young copse round the dead trunk has grown up from these rootsuckers. The distribution over very large intervals of sea, however, no doubt takes place in *Casuarina montana* and *C. equisetifolia* by means of the winged fruits, first through wind transport and then through ocean currents.

§ 5. On a monstrosity of Casuarina.

In the Herbarium at Leiden I found a specimen, which had been labelled by Boerlage as a monstrosity, collected by Junghuhn in Java [in H. L. B. sub. n. 50 (899—173)]. This malformation proved to be a fruiting branch, resembling a witches' broom (in German "Hexenbesen") and belonging to *Casuarina montana* var. *tenuior* Miq. Besides the above mentioned aberrant mode of branching, this specimen shows the peculiarity, that the axis of all its fruit cones has continued to grow. The axis, thus continued, gives the characteristic appearance to the shoots; are these branched like a witches' broom, have abnormally thickened internodes and bear abnormally developed leafsheaths. The shoots in question also bore a small number of normally formed young twigs and thus the determination was possible to me. These normal branches, have regular cylindrical internodes, about 1 cm. long and $^3/_4$—1 mm. thick, generally with 11 vaginal teeth, as is often the case in the above variety. I was unable to find a fungus or other cause for the formation of these witches'brooms in the herbarium-specimen referred to.

§ 6. Phyllogenetic note on Casuarina montana Jungh. and on C. equisetifolia Forst.

In the Herbaria at Leiden and at Utrecht I found herbarium-specimens of young seedlings and of very young shoots, developed from adventitious buds.

Accompanying one of the former specimens I found a manuscript note by Miquel, to the effect that these young seedlings had been raised from seed of *Casuarina montana*, imported in 1846 from Java to the Hortus at Rotterdam. These seedlings have on their youngest twigs internodes of about 2 mm. length and $^1/_3$ mm. diameter, with 4—5 deep grooves; in the 24 leaf sheaths examined by me, the number of vaginal teeth was as often 4 as 5, but never more and never less. The accompanying note of Miquel, indicates, however, that although 4—5 vaginal teeth were most common, he had also observed 6 teeth. The teeth are narrowly lanceolate and finely acuminate. The stems of these seedlings are only $2^1/_2$—3 mm. in diameter. Miquel has added in autograph: "Casuarina montana (*non* alior)" and below also *C. Brunoniana*. The species *C. Brunoniana*, which Miquel had described from young hot-house plants from the Rotterdam and Berlin Gardens, afterwards proved to be nothing but the "Jugendform" of *Casuarina equisetifolia* and *C. montana*. From two authentics of this species in the Herbarium at Utrecht, I could see that Miquel himself has withdrawn his *C. Brunoniana*, and regarded it partly as *C. equisetifolia* and partly as *C. montana*. It appears to me possible, however, that all the specimens named by Miquel *C. Brunoniana* belong to *C. montana* Jungh. only. For the young specimens, named by Miquel as *C. equisetifolia* agree well with this. Of young seedlings, which are derived with certainty from *C. equisetifolia*, I have here no material at my disposal for investigation. In Java I have only observed the constant unusually small number of vaginal teeth in young seedlings of *C. montana*, of the var. *tenuior*. In the very young seedlings I examined, the number was never more than 4—6 as in the seedlings of *C. Brunoniana* of the Utrecht Herbarium.

Concerning a herbarium specimen (Kds 37348 β in Herb. Lugd. Bat.) of *Casuarina montana* var. *tenuior* Miq., collected in Oct. 1899 at 2000 m. altitude near Ngadisari on Mt. Tengger in Eastern Java, I observed the following: The specimen consists of ordinary fertile old branches, and of some young sterile shoots, which had evidently developed from adventitious buds, after an older thicker trunk had been cut down near the ground. These young shoots were characterized by internodes of $^{1}/_{2}$ mm. diameter with 5—6 deep longitudinal grooves and only 5—6 vaginal teeth. On the other hand the youngest twigs, which had been formed on the ordinary ascending older branches of the same individual, had cylindrical internodes, not deeply-grooved, $^{3}/_{4}$—1 mm. diameter, with 9—10 vaginal teeth. For the sake of completeness the morphologically unimportant, but physiognomically striking circumstance should be mentioned, that a great number of the youngest twigs of these young root-suckers were malformed at their tops to ovate or irregularly formed galls, about 3—5 mm. long and $2^{1}/_{2}$—3 mm. thick. In these galls I could generally still detect the insect which had produced these malformations. It need scarcely be mentioned, that the above description of the morphologically aberrant structure of the twigs, refers only to normally constituted ones, and not to the pathological malformations on the rootsuckers, formed from adventitious buds. I may further allude to a specimen collected by Teysmann and De Vriese in 1859—1860 in Java? (without further indications as to locality) and labelled by Miquel "*Casuarina equisetifolia* Forst., *monstrosa?*" This specimen, found by me in the Herbarium at Leiden, appears to me to be quite similar to the one, described above, of the ordinary *Casuarina montana* var. *tenuior* Miq., with young root-suckers, partly deformed by galls at the shoot-tops, the number of vaginal teeth in this specimen, examined by Miquel is (also in the youngest twigs not attacked by galls) invariably only 6—7, never more.

Summing up (and wholly leaving out of account the above-described malformations due to galls) we find briefly the following:

1. In these very young seedlings of *Casuarina montana* var. *tenuior* Miq., some internodes are provided with 4, others with 5—6 deep longitudinal grooves, while the number of vaginal teeth is 4—6, (never more) and in the youngest stages only 4.

2. Very young shoots formed in *Casuarina montana* var. *tenuior* from adventitious buds in the base of the trunk, had similar deeper grooved internodes with 5—6 (never with more) vaginal teeth, like the young seedling mentioned sub 1.

3. It appears that in the species here in question (*C. montana*) the youngest developmental stages of the seedlings show phylogenetically older phases of development than the young shoots from adventitious buds of the trunk examined above.

4. The structure of the seedlings referred to sub 1 seems to point to both *Casuarina equisetifolia* Forst. and *C. montana* Jungh. being mutants of parent forms with quadrangular internodes and 4 deep longitudinal grooves, with 4 vaginal teeth. Such forms, which in my

opinion are older (e. g. *C. nodiflora* FORST. and *C. sumatrana* JUNGH.) still survive for instance, in Australia, in Sumatra, Borneo, Celebes, and in the Moluccas, but recent forms are now wanting in Java, and fossil ones have not yet been found in Java.

5. Of the two Javanese indigenous species of *Casuarina*, *C. montana* JUNGH. appear to be phylogenitically younger than *C. equisetifolia* FORST.; the former species is probably a mutant, which has only maintained itself within the region of the Malay Archipelago, and which has arisen from the latter species.

6. Probably *C. montana* var. *validior* MIQ. is a mutant, which has maintained itself in Java only and which has arisen from *C. montana* var. *tenuior* MIQ.

Physics. — "*Contribution to the theory of binary mixtures,*" XI. (Continued). By Prof. J. D. VAN DER WAALS.

Now we shall proceed to the investigation of some properties of the loci of the points of intersection of $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}=0$, in the first place when this locus is a closed figure, lying wholly at volumes larger than b. Let us write.

$$(v-b)^2+x(1-x)\left(\frac{db}{dx}\right)^2=x(1-x)\frac{c}{a}v^2$$

in the form:

$$v^2\left\{1-x(1-x)\frac{c}{a}\right\}-2vb+\left\{b_1{}^2+x(b_2{}^2-b_1{}^2)\right\}=0\,. \quad . \quad (\varphi)$$

The form of the third term in this equation appears only to depend on the first power of x, because $b^2+x(1-x)\left(\frac{db}{dx}\right)^2$ may be written $b_1{}^2+2xb_1\frac{db}{dx}+x^2\left(\frac{db}{dx}\right)^2$ and to this added $x(1-x)\left(\frac{db}{dx}\right)^2$. The third term then becomes $b_1{}^2+\frac{db}{dx}\left(2b_1+\frac{db}{dx}\right)x$, in which $\frac{db}{dx}=b_2-b_1$.

If we put $x(1-x)\frac{c}{a}=A$, the equation (φ) becomes

$$v^2(1-A)-2vb+b_1{}^2+x(b_2{}^2-b_1{}^2)=0 \quad . \quad . \quad . \quad (\varphi')$$

Let us seek the points of this line in which the tangent is parallel to the x-axis, and so in which $\frac{dv}{dx}=0$; then we find another equation by differentiating φ' with respect to x, and by keeping v constant, viz.:

$$-v^2\frac{dA}{dx}-2v\,(b_2-b_1)+b_2^2-b_1^2=0 \quad . \quad . \quad . \quad . \quad (\varphi'')$$

By eliminating v from (φ') and (φ''), we obtain an equation in x only — and for the values of x which satisfy this resulting equation, $\frac{dv}{dx}$ will be $=0$. We shall, however, seek a resulting equation in x in a somewhat different way.

If we subtract $x\,(\varphi'')$ from (φ'), we get:

$$v^2\left\{1-A+x\frac{dA}{dx}\right\}-2vb_1+b_1^2=0,$$

and adding this last equation to (φ''), we get:

$$v^2\left\{1-A-(1-x)\frac{dA}{dx}\right\}-2vb_2+b_2^2=0.$$

Hence:

$$\frac{b_1}{v}=1\pm\sqrt{\left\{A-x\frac{dA}{dx}\right\}}$$

and

$$\frac{b_2}{v}=1\pm\sqrt{\left\{A+(1-x)\frac{dA}{dx}\right\}}.$$

Now $\frac{b_1}{v}$ is certainly smaller than 1, hence in the expression for $\frac{b_1}{v}$ only the sign — can be retained before the radical sign. And leaving undecided for the present whether $v>b_2$ or $v<b_2$, we find when we divide $\frac{b_2}{v}$ by $\frac{b_1}{v}$:

$$n=\frac{1\pm\sqrt{\left\{A+(1-x)\frac{dA}{dx}\right\}}}{1-\sqrt{\left\{A-x\frac{dA}{dx}\right\}}}$$

or

$$n-1-n\sqrt{\left\{A-x\frac{dA}{dx}\right\}}\mp\sqrt{\left\{A+(1-x)\frac{dA}{dx}\right\}}=0. \quad (\varphi''')$$

Now

$$A+(1-x)\frac{dA}{dx}=(1-x)^2\frac{c}{a}\left\{1-\frac{x}{a}\frac{da}{dx}\right\}$$

and

$$A - x\frac{dA}{dx} = x^2 \frac{c}{a} 1 + \frac{1-x}{a}\frac{da}{dx}$$

The first member of equation (φ''') becomes for $x=0$:

$$n - 1 \mp \sqrt{\frac{c}{a_1}}\,.$$

or

$$n - 1 \mp \frac{n-1}{\sqrt{(1+\varepsilon_1)}}$$

and so, whether the sign — or the sign + is chosen, always positive, if as in the case considered, the quantity ε_1 is positive. For $x=1$ the first member of (φ''') becomes equal to:

$$(n-1) - n\sqrt{\frac{c}{a_2}}$$

or

$$n - 1 - \frac{n-1}{\sqrt{(1+\varepsilon_2)}}.$$

This value would be negative when, as will be supposed in a following case, ε_2 is negative — but it is also positive, if as is now the case, ε_2 is positive. If the sign of the value of the first member of (φ''') is different for $x=0$ and $x=1$, then there will be a value of x between 0 and 1 satisfying (φ'''). But in our case the first member of (φ''') has the same sign for $x=0$ and $x=1$. From this it does not follow, of course, that there exists no root for (φ'''), but only that this equation either has no roots or an even number. This equation has no roots when the locus is imaginary — but if the latter exists, as is the case when $1 > \frac{\sqrt{\varepsilon_1}+n\sqrt{\varepsilon_2}}{n-1}$, and when the locus is a closed figure, then there must be two. If the value of the first member of (φ''') is graphically represented between $x=0$ and $x=1$, the curve representing this value, begins and ends positive. If this value passes to negative values, it must have an ordinate equal to 0 at least twice, and so also assume a minimum value. Hence if there are two values of x satisfying (φ'''), the equation obtained by differentiating (φ''') with respect to x, must have a root. Now $\frac{d(\varphi''')}{dx}$ is equal to:

$$-\frac{n}{2}\frac{-x\dfrac{d^2A}{dx^2}}{\sqrt{\left\{A-x\dfrac{dA}{dx}\right\}}} \mp \frac{1}{2}\frac{(1-x)\dfrac{d^2A}{dx^2}}{\sqrt{\left\{A+(1-x)\dfrac{dA}{dx}\right\}}}.$$

So for the minimum value of (φ''') this equation must be equal to 0.

This expression is equal to 0, if $\frac{d^2A}{dx^2}=0$, or if:

$$\frac{nx}{\sqrt{\left(A-x\frac{dA}{dx}\right)}}=\pm\frac{1-x}{\sqrt{\left\{A+(1-x)\frac{dA}{dx}\right\}}}$$

The latter can only be the case, if in the second member the sign $+$ is retained, and $-$ is rejected. This means that in the expression:

$$n=\frac{1\pm\sqrt{\left\{A+(1-x)\frac{dA}{dx}\right\}}}{1-\sqrt{\left\{A-x\frac{dA}{dx}\right\}}}$$

only the sign $+$ must hold in the numerator of the second member, or that $\frac{b_2}{v}>1$. So if the closed curve is restricted to volumes smaller than b_2.

If we seek the value of x which satisfies:

$$\frac{n^2x^2}{A-x\frac{dA}{dx}}=\frac{(1-x)}{A+(1-x)\frac{dA}{dx}}$$

then when this value of x is substituted, (φ''') must be negative, because (φ''') has proved to be positive for $x=0$ and $x=1$.

For it is not sufficient for the existence of 2 roots of the equation $\varphi'''=1$ that φ''' has a minimum value, but it is also required that this minimum value is negative.

If we substitute in:

$$n-1-n\sqrt{\left\{A-x\frac{dA}{dx}\right\}}-\sqrt{\left\{A+(1-x)\frac{dA}{dx}\right\}}$$

the value of:

$$\sqrt{\left\{A-x\frac{dA}{dx}\right\}}=\frac{nx}{1-x}\sqrt{\left\{A+(1-x)\frac{dA}{dx}\right\}},$$

then:

$$n-1-\frac{n^2x+(1-x)}{1-x}\sqrt{\left\{A+(1-x)\frac{dA}{dx}\right\}}$$

must be negative.

Now we find from the condition on which φ''' has a minimum value:

$$\frac{dA}{dx}=A\frac{(1-x)^2-n^2x^2}{x(1-x)\{1-x+n^2x\}}$$

and

$$A + (1-x)\frac{dA}{dx} = A\frac{(1-x)^2}{(1-x+n^2x)x(1-x)} = \frac{c}{a}\frac{(1-x)^2}{1-x+n^2x}$$

Hence

$$(n-1) - \sqrt{\frac{c}{a}\{1-x+n^2x\}}$$

must be negative.

Now if we write $a = a_1(1-x) + a_2x - cx(1-x)$ and $\frac{a_1}{c} = \frac{1+\varepsilon_1}{(n-1)^2}$ and $\frac{a_2}{c} = n^2\frac{1+\varepsilon_2}{(n-1)^2}$, then

$$(n-1) - (n-1)\sqrt{\frac{1-x+x^2x}{(1-x)(1+\varepsilon_1)+xn^2(1+\varepsilon_2)-(n-1)^2x(1-x)}}$$

must be negative. This will be the case if under the radical sign the numerator is larger than the denominator, or if:

$$(1-x)(1+\varepsilon_1) + n^2x(1+\varepsilon_2) - (n-1)^2x(1-x) < 1-x+n^2x$$

or

$$(1-x)\varepsilon_1 + n^2x\varepsilon_2 - (n-1)^2x(1-x) < 0$$

or

$$\frac{\varepsilon_1}{(n-1)^2} - x\left\{1+\frac{\varepsilon_1-n^2\varepsilon_2}{(n-1)^2}\right\} + x^2 < 0.$$

The extreme values of x of the closed curve are given by the equation:

$$\frac{\varepsilon_1}{(n-1)^2} - x\left\{1+\frac{\varepsilon_1-n^2\varepsilon_2}{(n-1)^2}\right\} + x^2 = 0.$$

If the first member of this equation is negative, the values of x satisfying the same value, are nearer together, as was to be expected.

We have reduced the condition that ψ''' be negative in its minimum value to:

$$\frac{\varepsilon_1}{(n-1)^2} - x\left\{1+\frac{\varepsilon_1-n^2\varepsilon_2}{(n-1)^2}\right\} + x^2 = -\Delta,$$

if $\angle$ is a positive quantity. If this is to be the case for real values of x, then (ε_1 and ε_2 positive),

$$\left\{1+\frac{\varepsilon_1-n^2\varepsilon_2}{(n-1)^2}\right\}^2 > \frac{\varepsilon_1}{(n-1)^2}$$

must be, or

$$1 - \frac{\sqrt{\varepsilon_1} + x\sqrt{\varepsilon_2}}{n-1} > 0.$$

This condition is fulfilled when the points of which ε_1 and ε_2 are the coordinates, lie in the region for which the locus considered is a closed curve.

So we may sum up what has been demonstrated as follows. We have derived $\frac{(d\varphi''')}{dx}=0$ from $(\varphi''')=0$, and stated the condition on which φ''' becomes negative by the substitution of $\frac{d\varphi'''}{dx}=0$. Strictly speaking we should still have to show that $\frac{d\varphi'''}{dx}=0$ has real roots — and moreover that the value of these roots is in accordance with the result obtained. Let us, for this purpose, examine what follows concerning the value of x which satisfies the equation obtained before, which we derived from $\frac{d\varphi'''}{dx}=0$, viz.:

$$\frac{dA}{dx}=A\frac{(1-x)^2-n^2x^2}{x(1-x)\,[1-x+n^2x]}$$

Now $\frac{dA}{dx}=\frac{c[a_1(1-x)^2-a_2x^2]}{a^2}$ and $A=\frac{cx(1-x)}{a^2}$ and after reduction we find:

$$\frac{-a_1n^2+a_2}{c}=(1-x)^2-n^2x^2$$

or

$$\frac{n^2(\varepsilon_2-\varepsilon_1)}{(n-1)^2}=(1-x)^2-n^2x^2$$

For x between 0 and 1 the second member of this equation has a value of n which descends continually and lies between 0 and $-n^2$. So there will be a root if $\frac{n^2(\varepsilon_2-\varepsilon_1)}{(n-1)^2}<1$ and $>-n^2$. Or if

$$\varepsilon_1>\varepsilon_2-\left(\frac{n-1}{n}\right)^2$$

and

$$\varepsilon_1<\varepsilon_2+(n-1)^2$$

If we trace two lines at an angle of 45° with the axes through the points P and Q, then $\varepsilon_1<\varepsilon_2+(n-1)^2$ and $\varepsilon_1>\varepsilon_2-\frac{(n-1)^2}{x^2}$ implies that $\frac{dA}{dx}$ has one real root between $x=0$ and $x=1$ for all points between these two lines. If we confine ourselves to positive values of ε_1 and ε_2, this space comprises a very large part of the first parabola, and moreover the space which I shall indicate by OPQ

between the parabola and the axes. If we put $(1-x)^2 = \frac{n^2\varepsilon_2 + k}{(n-1)^2}$ and $n^2x^2 = \frac{n^2\varepsilon_1 + k}{(n-1)^2}$, these two equations, when k has been properly determined, will hold for the value of x of the root. By application of $(1-x) + x = 1$, we bring the condition for the determination of k in the following form:

$$\frac{n\sqrt{\left(\varepsilon_2 + \frac{k}{n^2}\right)}}{n-1} + \frac{\sqrt{\varepsilon_1 + \frac{k}{n^2}}}{n-1} = 1.$$

If for the binary mixture ε_1 and ε_2 were such that:

$$\frac{n\sqrt{\varepsilon_2}}{n-1} + \frac{\sqrt{\varepsilon_1}}{n-1} = 1$$

the point $(\varepsilon_1, \varepsilon_2)$ lies on the parabola, and the whole locus reduces to a point. But then it appears that for the root of $\frac{d(\varphi''')}{dx} = 0$ the quantity k must be $= 0$, and that the value of x for this root coincides with the point in which the locus has contracted. If ε_1 and ε_2 have such a value that $\frac{n\sqrt{\varepsilon_2}}{n-1} + \frac{\sqrt{\varepsilon_1}}{n-1} < 1$, the point $\varepsilon_1, \varepsilon_2$ lies in the space OPQ, and there is a locus between two values x_1 and x_2. If we add $\frac{k}{n^2}$ both to ε_1 and to ε_2, then $\frac{k}{n^2}$ may be chosen in such a way that the condition $\frac{d(\varphi''')}{dx} = 0$ is satisfied, and so also:

$$\frac{n\sqrt{\varepsilon_2 + \frac{k}{n^2}}}{n-1} + \frac{\sqrt{\varepsilon_1 + \frac{k}{n^2}}}{n-1} = 1$$

The addition of an equal amount to ε_1 and to ε_2 involves, of course, a shifting of the point $(\varepsilon_1, \varepsilon_2)$ in a direction which makes an angle of 45° with the axes, and that in such a way that the projection of the shifting on each of the axes is equal to $\frac{k}{n^2}$. We suppose k to be positive. So we find the value of k by taking n^2 times the amount which is to be added to the projections of the said point to reach the parabola. If the point $(\varepsilon_1, \varepsilon_2)$ lies in OPQ, k is positive. But for points within the parabola, k is negative. But as for the case that the closed locus exists, the point $(\varepsilon_1, \varepsilon_2)$ must lie inside OPQ, we have only to deal with positive values of k.

So we have $x > \frac{\sqrt{\varepsilon_1}}{n-1}$ and $1 - x > \frac{n\sqrt{\varepsilon_2}}{n-1}$, and the equation:

$$\frac{\frac{\varepsilon_1}{(n-1)^2}}{x} + \frac{\frac{n^2\varepsilon_2}{(n-1)^2}}{1-x} = 1$$

holding for the values of x of the points of the locus, we find, after substitution of $x > \frac{\sqrt{\varepsilon_1}}{n-1}$ and $1 - x > \frac{n\sqrt{\varepsilon_2}}{n-1}$:

$$\frac{\sqrt{\varepsilon_1}}{n-1} + \frac{n\sqrt{\varepsilon_2}}{n-1} < 1$$

a relation which exists indeed for points of the space OPQ below the parabola.

But now we have to make the following remark about the equation which indicates the value of x for the points where $\frac{dv}{dx} = 0$ for the closed curve. For this equation (φ''') we found the following form:

$$n - 1 - n\sqrt{\left\{A - x\frac{dA}{dx}\right\}} \mp \sqrt{\left\{A + (1-x)\frac{dA}{dx}\right\}} = 0$$

or

$$(n-1) - nx\sqrt{\frac{c}{a}}\left\{1 + \frac{1-x}{a}\frac{da}{dx}\right\} \mp (1-x)\sqrt{\frac{c}{a}}\left\{1 - \frac{x}{a}\frac{da}{dx}\right\} = 0.$$

If we seek the values of $\frac{a + (1-x)\frac{da}{dx}}{a}$ and of $\frac{a - x\frac{da}{dx}}{a}$, we find $\frac{a_2 - c(1-x)^2}{a}$ and $\frac{a_1 - cx^2}{a}$ for this. These quantities must be positive, because they occur under the radical sign. And this gives a restriction for the values of x for which $\frac{dv}{dx}$ can be $= 0$. If $a_2 > c$ the former of the values mentioned is positive for all the values from $x = 0$ to $x = 1$. The quantity $\frac{a_2}{c}$ is equal to $\frac{n^2(1+\varepsilon_2)}{(n-1)^2}$, and so certainly greater than 1 for positive ε_2. The quantity $a_1 - cx^2$ is positive, when $x^2 < \frac{a_1}{c}$ and negative for $x^2 > \frac{a_1}{c}$. So if $\frac{a_1}{c} < 1$, values of x lying near 1, cannot exist. This will be the case, as soon as $1 > \frac{a_1}{c}$ or $1 > \frac{1+\varepsilon_1}{(n-1)^2}$, or $n^2 - 2n > \varepsilon_1$. If we put the greatest value of x at which $\frac{dv}{dx} = 0$ can still occur $= x_g$, then $1 + \varepsilon_1 = x_g^2 (n-1)^2$ $\varepsilon_1 = x_g^2 (n-1)^2 - 1$, which value must be positive for ε_1.

Now we may proceed to demonstrate that the minimum of (φ''') cannot be given by the second factor of $\frac{d(\varphi''')}{dx} = 0$, viz. by $\frac{d^2A}{dx^2} = 0$; and at the same time furnish a proof for the theorem that $\frac{dv}{dx} = 0$ can only occur for volumes smaller than b_2. The quantity $A = \frac{x(1-x)c}{a}$ begins with a value $= 0$ at $x = 0$, and ends also with 0 at $x = 1$. So there is a maximum value and we find it from $\frac{dA}{dx} = \frac{c\left[a_1 (1-x)^2 - a_2 x^2\right]}{a^2}$ at $\frac{x}{1-x} = \sqrt{\frac{a_1}{a_2}}$. For this maximum value of A $\frac{d^2A}{dx^2} < 0$, and we should be apt to suppose that this will be the case throughout the course from $x = 0$ to $x = 1$. This, however, is not always the case. In some cases a point of inflection appears in the line representing A at certain value of x, and then $\frac{d^2A}{dx^2}$ is positive for greater value of x. If we calculate $\frac{d^2A}{dx^2}$, we may reduce it to the following form:

$$\frac{d^2A}{dx^2} = -\frac{2c}{a^3}\left\{a_1a_2 - c\left[a_1 (1-x)^3 + a_2x^3\right]\right\}$$

And now it is the question whether $a_1a_2 - \left[a_1 (1-x)^3 + a_2x^3\right]$ can be equal to 0. For $x = 0$ this quantity is $a_1 \left[a_2 - c\right]$, and as $\frac{a_2}{c} = \frac{n^2 (1+\varepsilon_2)}{(n-1)^2}$, the value of $a_2 - c$ will certainly be positive for positive ε_2. Hence $\frac{d^2A}{dx^2}$ is negative for $x = 0$. For $x = 1$ this quantity is $a_2 (a_1 - c)$ and as $\frac{a_1}{c} = \frac{1+\varepsilon_1}{(n-1)^2}$ and $\frac{a_1}{c} - 1 = \frac{1+\varepsilon_1}{(n-1)^2} - 1$, we can get a negative value for it if the value of ε_1 is small and that of n large. This case occurs when $\varepsilon_1 < n^2 - 2n$. Then there is a value of x for which $\frac{d^2A}{dx^2}$ changes the negative sign into the positive one. Now we saw, however, above, that if $\varepsilon_1 < n^2 - 2n$, the value of $(\varphi''') = 0$ is not real over the full extent from $x = 0$ to $x = 1$. And now the question rises which value of x is greater: the value at which φ''' becomes imaginary or the value of x at which $\frac{d^2A}{dx^2}$ becomes $= 0$. We can decide this at once by substituting $x_g = \sqrt{\frac{a_1}{c}}$, the limiting value for (φ''') real, in $\frac{d^2A}{dx^2}$. We find then:

$$\frac{d^2A}{dx^2} = -2\frac{c^2}{a^3}\left\{\frac{a_1}{c}\frac{a_2}{c} - \left[\frac{a_1}{c}(1-x)^2 + \frac{a_2}{c}x^2\right]\right\} =$$

$$= -2\frac{c^2}{a^3}\left\{x_g^2\frac{a_2}{c} - x_g^2(1-x_g)^2 - x_g\frac{a_1}{c}\right\}$$

or

$$\frac{d^2A}{dx^2} = -\frac{2c^2}{a^3}x_g^2(1-x_g)\left\{\frac{a_2}{c} - (1-x_g)\right\}$$

As $\frac{a^2}{c} > 1$, and à fortiori $> (1-x_g)$, we find $\frac{d^2A}{dx^2}$ still negative.

Finally by availing ourselves of the values obtained we shall be able to verify that even if the function (φ''') is not real over the full extent from $x = 0$ to $x = 1$, and so if our conclusion that this function must possess a minimum value which is negative, can no longer be considered as proved, there is even in this case also a root for $\frac{d(\varphi'')}{dx} = 0$ at a value of x which is smaller than x_g, and which has therefore the former meaning for (φ''').

For the root of $\frac{d(\varphi''')}{dx} = 0$ holds the equation:

$$\frac{a_2 - n^2a_1}{c} = (1-x)^2 - n^2x^2 \text{ (see page 431)}$$

and so if $\frac{a_1}{c} = x_g^2$ is put, the following equation holds:

$$\frac{a_2}{c} - (1-x_g)^2 = (1-x)^2 - (1-x_g)^2 + n^2(x_g^2 - x^2)$$

or

$$\frac{a_2}{c} - (1-x_g)^2 = (x_g - x)\{2 + (n^2-1)(x_g + x)\}.$$

and as $\frac{a_2}{c} - (1-x_g)^2$ is positive, $(x_g - x)$ must also be positive, or the root of $\frac{d(\varphi''')}{dx} = 0$ lies at smaller value of x than that of the final point of (φ'''). At the final point $(\varphi''') = 0$. At $x = 0$, (φ''') is positive. So for the intermediate minimum value (φ''') is negative.

The function $\varphi''' = 0$, the relation through which we may know the value of x for the points in which $\frac{dv}{dx} = 0$ for the closed curve, must also be satisfied by the value of x of the point in which the closed curve has contracted to a single point. To show this we have to substitute the values $x = \frac{\sqrt{\varepsilon_1}}{n-1}$ and $(1-x) = \frac{\sqrt{\varepsilon_2}}{n-1}$ in:

$$(n-1) - nx\frac{c}{a}(1-x)\sqrt{\left[\frac{a_2}{c(1-x)^2} - 1\right]} - (1-x)\frac{xc}{a}\sqrt{\frac{a_2}{cx^2} - 1} = 0$$

where it appears that this equation is satisfied. That we only retain the sign — for the third term is in accordance with our conclusion that $v < b_2$ for the whole curve. And that $\frac{dv}{dx} = 0$ must also be satisfied in the isolated point, — the point to which the whole curve has contracted, — follows from the circumstance that for such a point $\frac{dv}{dx}$ has an arbitrary value. The quantity $\frac{a}{cx(1-x)} = \frac{1}{A}$ is equal to:

$$\frac{a_1(1-2(+a_2x - cx\,1-2)}{cx\,(1-x)} = \frac{a_1}{cx} + \frac{a_2}{c(1-x)} - 1 = \frac{1+\varepsilon_1}{(n-1)\sqrt{\varepsilon^1}} + \frac{n(1+\varepsilon_2)}{(n-1)\sqrt{\varepsilon_2}} - 1$$

or

$$\frac{a}{cx(1-x)} = \frac{\frac{1}{\sqrt{\varepsilon_1}} + \frac{n}{\sqrt{\varepsilon_2}}}{n-1}$$

Further $\sqrt{\frac{a_2}{c(1-x)^2} - 1} = \sqrt{\frac{1}{\varepsilon_2}}$ and $\sqrt{\frac{a_1}{cx^3} - 1} = \sqrt{\frac{1}{\varepsilon_1}}$.

Substituting these values we find:

$$(n-1) - \frac{(n-1)}{\frac{1}{\sqrt{\varepsilon_1}} + \frac{n}{\sqrt{\varepsilon_2}}}\left[\frac{n}{\sqrt{\varepsilon_2}} + \frac{1}{\sqrt{\varepsilon_1}}\right] = 0$$

Let us write the equation of the closed curve in the following form:

$$\left(\frac{v}{b}\right)^2(1-A) - 2\frac{v}{b} + (1+B) = 0,$$

representing by B $\frac{\left(\frac{db}{dx}\right)^2 x(1-x)}{b^2} = \frac{(n-1)^2\,x\,(1-x)}{(1-x)^2 + 2nx\,(1-x) + n^2x^2}$.

Let us seek the points of this curve for which $\frac{d\frac{v}{b}}{dx} = 0$. Such a point lies for the branch of the small volumes on the right of the point for which $\frac{dv}{dx} = 0$, and on the left for the branch of the larger volumes. By differentiating the equation of the curve in the last mentioned form with respect to x, and keeping $\frac{v}{b}$ constant, we find as a condition:

$$-\left(\frac{v}{b}\right)^2 \frac{dA}{dx} + \frac{dB}{dx} = 0,$$

or

$$\frac{v}{b} = + \frac{\sqrt{\frac{dB}{dx}}}{\sqrt{\frac{dA}{dx}}},$$

from which it appears that $\frac{dA}{dx}$ and $\frac{dB}{dx}$ must have the same sign for such points. Now $\frac{dA}{dx} = \frac{c\{a_1(1-x)^2 - a_2x^2\}}{a^2}$ and for $\frac{dB}{dx}$ we find the value $\frac{(n-1)^2\{(1-x)^2 - n^2x^2\}}{(1-x+nx)^4}$. So $\frac{1-x}{x} \lessgtr \sqrt{\frac{a_1}{a_2}}$ must go together with $\frac{1-x}{x} \lessgtr \frac{1}{n}$; or $\frac{x}{1-x} \lessgtr \frac{1}{n}$ and $\frac{x}{1-x} \lessgtr \frac{1}{n}\sqrt{\frac{1+\varepsilon_1}{1+\varepsilon_2}}$ must hold at the same time. What it depends on whether $\frac{dB}{dx}$ and $\frac{dA}{dx}$ is positive or negative, is seen when the value obtained for $\frac{v}{b}$ is substituted in the equation of the curve. If we write this as follows:

$$\left(\frac{v}{b} - 1\right)^2 = A\left(\frac{v}{b}\right)^2 - B$$

we find:

$$\left(\sqrt{\frac{\frac{dB}{dx}}{\frac{dA}{dx}}} - 1\right) = \pm \sqrt{\frac{A\frac{dB}{dx} - B}{\frac{dA}{dx}}}$$

or

$$\left(\sqrt{\frac{\frac{dB}{dx}}{\frac{dA}{dx}}}-1\right)=\sqrt{\frac{A^2}{\frac{dA}{dx}}\frac{d\left(\frac{B}{A}\right)}{dx}}$$

And as $\frac{B}{A}=\frac{(b_2-b_1)^2}{c}\frac{a}{b^2}$ and $\frac{a}{b^2}=27\,p_{kr}$, it appears that $\frac{dA}{dx}$ and so also $\frac{dB}{dx}$ have the same sign as $\frac{dp_{kr}}{dx}$. So if $\frac{a_2}{b_2^2}>\frac{a_1}{b_1^2}$ or $\varepsilon_2>\varepsilon_1$, then $\frac{dA}{dx}$ and $\frac{dB}{dx}$ is positive, and vice versa. The line which divides the angle between the axes into two equal parts in fig. 36 or joins point O' with point O in fig. 37, gives the division between $\varepsilon_2 \gtrless \varepsilon_1$. For $\frac{dp_{kr}}{dx}>0$, $p_{kr_2}>p_{kr_1}$ or $\frac{a_2}{b_2^2}>\frac{a_1}{b_1^2}$ and $\varepsilon_2>\varepsilon_1$. This is the case for all points lying right of this line — and the other way about. For the points of this line themselves $\varepsilon_2=\varepsilon_1$ or $\frac{dp_{kr}}{dx}=0$. But then also $\frac{dA}{dx}$ and $\frac{dB}{dx}=0$ and so $\frac{x}{1-x}=\frac{1}{n}$, or what is the same thing

$$\frac{x}{1-x}=\sqrt{\frac{a_1}{a_2}}=\frac{1}{n}\sqrt{\frac{1+\varepsilon_1}{1+\varepsilon_2}}$$

But, as we already observed above, this requires that the value l^2 be greater than 1 in the formula $l^2n^2(1+\varepsilon_1)^2=\left[n+\frac{1+n^2}{2}\varepsilon_1\right]$ or $l\,n(1+\varepsilon_1)=n\frac{1+n^2}{2}\varepsilon_1$. Then we have:

$$l=\frac{1+\frac{1+n^2}{2n}\varepsilon_1}{1+\varepsilon_1}$$

or

$$l-1=\frac{(n-1)^2}{2n(1+\varepsilon_1)}\varepsilon_1\,.$$

Now for the area OPQ, under the parabola we have

$$(1+n)\sqrt{\varepsilon_1}\leqq n-1$$

and so ε_1 can become equal to $\left(\frac{n-1}{n+1}\right)^2$ as highest value, and hence $(l-1)_{max}=\frac{(n-1)^4}{4n(n^2+1)}$. For not very high value of n, $l-1$ is only small. So $l-1$ is equal to $\frac{1}{40}$ e.g. for $n=2$. For $n=3, l-1=\frac{2}{15}$ But this is no longer the case for high value of n. We need not fear in any case, however, that l will become so great that $a_1+a_2-2\,a_{12}$ would become <0. That c be >0, the following equation must hold:

$$2\,a_{12} < a_1 + a_2$$

or

$$2\,l\sqrt{a_1\,a_2} < a_1 + a_2$$

or

$$2\,l < \sqrt{\frac{a_1}{a_2}} + \sqrt{\frac{a_2}{a_1}}$$

or

$$2\,l < \frac{1}{n}\sqrt{\frac{1+\varepsilon_1}{1+\varepsilon_2}} + n\sqrt{\frac{1+\varepsilon_2}{1+\varepsilon_1}}\,.$$

or in our case

$$2l < n + \frac{1}{n}$$

or

$$(l-1) < \frac{(n-1)^2}{2n}$$

Now

$$(l-1) = \frac{(n-1)^2}{2n} - \frac{\varepsilon_1}{1+\varepsilon_1}\,.$$

Hence $(l-1)_{max}$ remains also below the value, which would make $a_1+a_2-2a_{12}$ equal to 0.

But now before proceeding to the comparison of the results obtained here with those of the experiment, I shall first have to discuss the question whether the disappearance of the intersection of $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}=0$ really involves the disappearance of the complication in the spinodal line, — and so whether the temperature at which the two curves mentioned touch, is at the same time the temperature at which the pair of *heterogeneous* plaitpoints occurring in the spinodal line, coincide. When the points of intersection of the two curves approach each other, the two *heterogeneous* plaitpoints will, no doubt, also come nearer to each other. But it need not follow from this that when the points of intersection coincide, also the pair of plaitpoints coincide. And à priori it is unlikely that this should be the case. The existence or non-existence of points of intersection depends only on properties of the two curves, without a third curve

$\frac{d^2\psi}{dxdv} = 0$ being able to exert any influence on this. But the course of the spinodal line is the result of properties of $\frac{d^2\psi}{dx^2} = 0$ as well as of $\frac{d^2\psi}{dv^2} = 0$ and of $\frac{d^2\psi}{dxdv} = 0$; from this it may already be expected that when the curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ touch, the two *heterogeneous* plaitpoints will occur on the spinodal line, and will lie at some distance from each other. If this is so, this means that the limits for the existence and disappearance of the heterogeneous plaitpoints are wider apart than the temperatures at which the two curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ begin to intersect and stop doing so; and à fortiori this is the case for the limits of the temperature of their appearance and disappearance on the binodal line, and so also for the limits of the temperature for the existence of three-phase-pressure. And that this is true may be seen when we more closely examine the peculiarities which occur in the course of the spinodal line in the case that the two curves still intersect. Let us imagine the circumstances as in fig. 12, Vol. IX, p. 846, Contribution III, viz. the line $\frac{dp}{dx_v} = 0$ at smaller volume than the line $\frac{dp}{dv} = 0$; but preferably at somewhat lower temperature, so that at $x = 0$ the two branches of $\frac{dp}{dv} = 0$ are still separated.

Then the isobars enter the figure at $x = 1$, have $\frac{dv}{dx_p}$ negative, and in the neighbourhood of $\frac{dp}{dv} = 0$ they incline towards this curve which they intersect in a direction parallel to the axis of v. So the quantity $\frac{d^2v}{dx^2_p}$ is positive. For the q-lines the quantity $\frac{d^2v}{dx^2_q}$ is negative in the neighbourhood of $\frac{dp}{dv} = 0$. So in a point of contact of the p- and q-lines, a point of the spinodal line (see Vol. IX p. 747 Contr. II), $\left(\frac{dv}{dx}\right)_{spin}$ is positive according to the formula:

$$\left(\frac{dv}{dx}\right)_{spin} = \left(\frac{dv}{dx}\right)_{p=q} \frac{\left(\frac{d^2v}{dx^2}\right)_q}{\left(\frac{d^2v}{dx^2}\right)_p}$$

And according to the formula Vol. IX p. 749, Contribution II):

$$\left(\frac{dp}{dx}\right)_{spin} = \left(\frac{dp}{dx}\right)_v \left\{ 1 - \frac{\left(\frac{d^2v}{dx^2}\right)_q}{\left(\frac{d^2v}{dx^2}\right)_p} \right\}$$

$\left(\frac{dp}{dx}\right)_{spin}$ has the same sign as $\left(\frac{dp}{dx}\right)_v$, and is therefore negative. In the point of contact the two lines p and q do not intersect. The p-line lies in the point of contact on the same side of the q-line — e. g. on the lower side. But in fig. 12 contact of a p- and a q line has again been drawn on the left side of $\frac{d^2\psi}{dx^2} = 0$. But there the p-line remains above the q-line all through. So there must be a point of contact somewhere between, where there is a transition between these two cases, and where the contact is at the same time intersection. Then not only $\frac{dv}{dx_p} = \frac{dv}{dx_q}$, but $\frac{d^2v}{dx^2_p} = \frac{d^2v}{dx^2_q}$ and so also $\frac{dp}{dx} = 0$. Then we are in a plaitpoint. If taking due account of the course of the p- and q-lines, we seek this plaitpoint it appears that this point does not lie on that particular q-line that passes through the highest point of the curve $\frac{d^2\psi}{dx^2} = 0$, and has there a direction parallel to the x-axis, and also possesses there a point of inflection. But it lies on a q-line lying left of the former, where p has a greater value; while this plaitpoint must lie below the point of inflection of the q-line, because $\frac{d^2v}{dx^2_p}$ is always positive.

Of course, but this is not necessary for our argument, if for points of the spinodal line with very small x, the contact of the q- and p-lines is to take place again in such a way that the p-line remains again throughout on the same side of the p-line, which we may also call the lower side, there must exist another plaitpoint also on the left hand of $\frac{d^2\psi}{dx^2} = 0$. So in this second plaitpoint the p-line, coming from the right, must first run above the q-line, which it will touch, and will be below it from the point of contact. What is indeed essential for our argument, is the circumstance that the first-mentioned plaitpoint, the upper of the pair of heterogeneous plaitpoints, which I called the realizable one in a previous Contribution, though it only fully deserves this name when it also lies above the binodal curve, lies on an isobar of higher value of the pressure than the value of p found in the point in which $\frac{d^2\psi}{dx^2} = 0$ has the smallest volume. And if we now consider the case that the whole closed curve discussed above, has contracted to a single point, and the intersection of the two curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dx^2}$ has disappeared, and the q-line runs parallel to the x-axis in that single point and possesses there a point of inflection, the realizable plaitpoint still exists, and so also the other, the hidden one. A fortiori this is the case when the closed curve still exists, and the intersection of the two curves, $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ has only disappeared because they touch. For then the q-line, which passes through the point of contact, will still possess the points with maximum and minimum volume, and it will lie below the q-line where they have coincided.

So we are justified in the following graphical representation. Let us take an x-axis and a p-axis. Let us construct a figure indicating first the pressure along the liquid branch of the line $\frac{d^2\psi}{dv^2} = 0$, and secondly the pressure along the liquid branch of the spinodal line. Not to interrupt our train of reasoning too much, we shall pass over the other branches in silence, and moreover confine ourselves to the case in which $T_{k_2} > T_{k_1}$. Then the first-mentioned line is a continually descending one. If the temperatures are low — according to the approximate equation of state below $^{27}/_{32}\ T_k$ — all the points of this line lie below the x-axis. But as we only wish to consider the relative position of the two curves which are to be represented we disregard the absolute height at which we think them drawn. The second line begins and terminates as high as the first, and always remains above it. So in the main it is also a fast descending line. Now if there are on the first line two points, indicating the points of intersection of the line $\frac{dp}{dx} = 0$ with $\frac{d^2\psi}{dx^3} = 0$, the second line will not continually descend, but possess a minimum and a maximum value for p. The minimum value at a value of x which is smaller than the value of x of the first point of intersection, and the maximum value at a value of x, which is greater than that of the second point of intersection. This minimum and this maximum value are those of the pair of *heterogeneous* plaitpoints. If the two points of intersection have coincided on the first-mentioned line, minimum and maximum pressure still occurs on the second. And only at a temperature, at which either there is not yet question of contact of the two curves $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}$, or at which this contact is long over, the complication in the course of the p-line will have disappeared for the spinodal line. At the moment of the disappearance this p-line possesses a horizontal tangent and a point of inflection in the point in which maximum and minimum pressure coincide. If further in such a figure we drew a third line indicating the pressure along the binodal curve, this third line would have a complicated shape — but for this I refer to some Communications occurring in These Proceedings 1905.

But from all this we further conclude that is not necessary that the two curves $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}=0$ intersect for the occurrence of the pair of heterogeneous plaitpoints on the spinodal line. If they only draw near enough to each other, the spinodal line can already possess the described complication, and there can even be three-phase-pressure.

It follows from this that for mixtures the properties of whose components are represented besides by n, by positive ε_1 and ε_2, the presence of the heterogeneous plaitpoints is not restricted to the space OPQ below the parabola for ε_1 and ε_2; but that this space must be extended with a part of the parabola itself — a part lying in the neighbourhood of the top. The theoretically exact shape of this part can only be determined by investigation of the spinodal line itself. But in view of the difficulties attending this investigation, I shall content myself here with an indication of the way in which I have tried to form an idea for myself of the accuracy of my expectations that this part would again be approximately bounded by a parabola, which compared to the preceding one, would have shifted in the direction of the axis, though what follows must not be looked upon as much more than a certain kind of empirical calculation. When the curve $\frac{d^2\psi}{dx^2}=0$ lies entirely within $\frac{d^2\psi}{dv^2}=0$, but in the neigbourhood of the latter curve, two other curves, viz. $\frac{d^2\psi}{dv^2}=0$ at lower temperature, and $\frac{d^2\psi}{dx^2}=0$ at another still lower temperature will show intersection and contact in the space outside $\frac{d^2\psi}{dv^2}=0$, where the spinodal curve lies, and where the pair of heterogeneous plaitpoints are found, at a certain distance apart or coinciding.

If in $\frac{d^2\psi}{dv^2}=0$ we take the lower temperature $T''=\frac{T}{k}$, and in $\frac{d^2\psi}{dx^2}=0$ the value of the lower temperature $T'''=\frac{T}{k'}$, we obtain by elimination of T, the equation, which with a slight modification agrees with (2) of Contribution X:

$$v^2\left\{1-x(1-x)\frac{k'}{k}\frac{\frac{d^2a}{dx^2}}{2a}\right\}-2bv+\left\{b^2+x(1-x)\left(\frac{db}{dx}\right)^2\right\}=0.$$

If we now treat this equation in the same way as (a) was treated in Contribution X, we get, for the case that the closed curve contracts to one point, the condition:

$$n-1=\sqrt{\left(\varepsilon_1-\frac{k'-k}{k}\right)}+n\sqrt{\left(\varepsilon_2-\frac{k'-k}{k}\right)}.$$

So the same parabola as before, only shifted in the direction of the two axes by an amount equal to $\frac{k'-k}{k}$.

The value of T at which the imitated plaitpoints coincide in this calculation, is now k or k' times higher.

(*To be continued*).

E R R A T U M.

In the proof that the closed curve, the locus of the points of intersection of $\frac{d^2\psi}{dv^2}=0$ and $\frac{d^2\psi}{dx^2}=0$, always lies at $v<b_2$, a possible case has been overlooked. The value $v<b_2$ may occur if:

$$n-1>\sqrt{1+\varepsilon_1}+n\sqrt{\varepsilon_2}\,,$$

as will be shown in the *Continuation.*

(December 23, 1908).

KONINKLIJKE AKADEMIE
VAN WETENSCHAPPEN
-:- TE AMSTERDAM -:-

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PROCEEDINGS OF THE MEETING
of Thursday December 24, 1908.

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Botany. — "*On the biological significance of the secretion of nectar in the flower.*" By Dr. W. Burck.

(Communicated in the meeting of November 28 1908.)

In an article in the Recueil des travaux botaniques Néerlandais vol. IV.[1]) I have explained in detail, that Darwin in 1859 put forward the hypothesis, that a cross with another individual is indispensable for the species and that, at the time, he considered the structure of flowers to be generally such as to ensure, or at least to favour, cross-fertilisation, but that in later years he, however, left this stand-point. I showed from his later writings, that the observations and experiments of many years had brought him more and more to the conclusion, that a much greater significance should be attached to self-fertilisation, than he had at first imagined; I also showed that, at the close of his studies, he was not very far from giving a negative answer to the question whether floral structure favours cross-fertilisation. Since then, observations have been made on a number of tropical plants, the flowers of which are always closed, so that in such plants the possibility of cross-fertilisation is excluded and I further pointed out, that from these results there can be no question of a natural law in the sense imagined by DARWIN. Furthermore, the view that cross-fertilisation might be advantageous to the species, has been rendered untenable by our present knowledge of the structure of the nucleus, and its function in the life of the plant, and also by our modern ideas concerning the nature of fertilisation.

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[1]) An abstract of this may be found in Biolog. Centralblatt. Bd. XXVIII. N⁰. 6. 1908.

Suppose we now give up this view, and fall back on the fundamental hypothesis, which was put forward by GÄRTNER in 1849, that only by self-fertilisation, vigour and fertility of the species are preserved, since a cross may lead to hybrid-formation, which diminishes the fertility of the plant. It then follows, that floral biology, which has started in its considerations from the opposite view, has lost its basis and must be built up anew. We have been led astray by our ideas regarding the significance of the properties of the perianth — its shape and dimensions, its colour and odour — and regarding the various mechanisms of the flower — dioecism, monoecism, heterogamy, dichogamy, hercogamy and self-sterility — all of which we thought we could explain as useful adaptations for visiting insects in order to ensure cross-fertilisation; it must be possible to explain them in another way. I have already shown in my previous paper that diclinism and hercogamy can be explained by *mutation* and that protandry and protogyny must be considered as characters of organisation, and not of adaptation.

With regard to the phenomenon of self-sterility I limited myself to pointing out, that this should be considered primarily as the result of hybridisation, rather than as a special adaptation.

In order that we may now obtain a better conception of the qualities of the floral envelopes, we must again adopt the view of the older biologists, who regarded these envelopes as organs for the protection of the sexual apparatus.

We must therefore consider to what extent the sexual organs require the protection of the perianth, not only when they originate and develop, but also during the flowering period. Hitherto we have been accustomed to look for a connexion between the various properties of the perianth and its significance in the attraction of insects. Now we shall have to test these same properties, especially of shape, dimension, position and the distribution of fragrant vapours, by the question, how they may be considered to be of importance to an organ, which is intended to protect the sexual organs from unfavourable external influences. More than has hitherto been the custom in floral biology, we shall have to pay attention to the anatomical structure and the physical and chemical properties of the floral envelopes, to the way in which the floral leaves are arranged in the bud, with reference to each other, (the aestivation) to mutual coalescence, to the presence of scales, hairs and glands, to the secretion of water, honey, mucilage, etc. Also, if we give prominence to the protection of the generative organs as the basis of our considerations, we shall have to investigate whether the *secretion of nectar* is not connected with this protective function.

This connexion may be inferred all the more readily on account of the unmistakable correspondence of the secretion of nectar during the flowering period to that of water or of a mucilaginous fluid in the so-called water-calyces, the latter secretion being considered a means of protection of the sexual organs.

With regard to this secretion of water I beg to recall, that 20 years ago TREUB first drew attention to the remarkable phenomenon that the floral buds of *Spathodea campanulata* BEAUV., a tropical *Bignoniacea*, are filled with a watery liquid, secreted by a large number of glands, which cover the inner surface of the calyx, so that the petals, stamens and ovaries develop under the protection of this fluid. The liquid contains traces of the hydrochlorides, carbonates, nitrates and sulphates of potassium, sodium and calcium, has an alkaline reaction and contains traces of ammonia; sugar was not found in it.

A similar secretion of water in the closed flower-bud was afterwards also observed in other plants. We may mention the papers of LAGERHEIM, GREGOR KRAUS, HALLIER, KOORDERS, SHIBATA and SVEDELIUS, to whose investigations I do not propose to refer here in further detail, as I intend to publish my own observations on this subject before long. From these it will be evident, that the phenomenon is not limited to the tropics, but can also be studied here.

I only wish to emphasize, however, that all naturalists, who have occupied themselves with the subject, have accepted the opinion of TREUB, that the secretion of water is a means of protecting the sexual organs against the unfavourable consequences of too strong transpiration, and that my personal observations, especially in this country, have shown me the connexion between the secretion of water and of nectar, and have gradually confirmed me in the conviction, that by the nectar-secretion the sexual organs are protected.

I wish briefly to explain the train of thought, from which I started my investigation.

The observations on plants with water-calyx and especially the detailed investigations of KOORDERS have taught us, that already long before the corolla and the sexual organs are laid down, the very young calyx (the development of which in all these plants is hurried on, before that of the other parts of the flower) is protected against the dangers of exposure to the atmosphere; sometimes the calyx is protected by glands, which may or may not be active, sometimes by a thick covering of hairs, which retains air, sometimes by both these means. It is intelligible, that this young organ, the vascular bundles of which are as yet unperfectly developed and therefore unable to compensate adequately for the loss of water through transpiration, should require a special, temporary protection, in so far as it is not surrounded by bracts.

Now we see at a later stage, in which the calyx has already acquired certain dimensions and in which its anatomical structure is nearing completion, that the same glands appear on the *inner surface*, and by their activity more or less fill the cavity of the calyx with water; this secretion of water supplements the protective function of the calyx towards the other parts of the flower, which are now beginning their development.

Later, in older buds, when the stamens and ovaries have already made considerable progress, the same glands appear on the outer- and on the inner surface of the *corolla*. The former, the *outer* glands, are especially active in protecting the petals against excessive transpiration in the short period, between the bursting open of the calyx and the development of the petals to their full size — temporarily therefore [1]. The significance of the hairs on the *inner surface* would then be, that in the same period they keep the sexual organs in a moist space.

When we see therefore, that the flower is carefully protected against transpiration from the first stages of its development to the moment of opening, the question naturally arises, whether at the opening and during the flowering-period, the sexual organs are under such especially favourable conditions, that they require no protection?

This is certainly not the case; during the flowering period the ovary is not placed in favourable conditions.

When opening, the flower enters upon a period, in which the stamens and the ovaries — exceptions apart — have reached their highest stage of development, do not require food for further growth and are in a state of rest; the ovaries are awaiting fertilisation in order to be called to new life by that stimulus; the stamens in a state of maturity, await the evaporation of the superfluous water from the anthers.

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[1] This opinion will later be supported by examples; I propose to show, that at this stage, when the corolla is still completely closed, water or nectar is found in many flowers.

At the opening of the flower the perianth, and especially the corolla, are in very different condition, the latter generally not having reached anything like its full size, when the sepals move apart. In a very short time, the corolla grows out to its normal dimensions, to be afterwards during the whole flowering period the seat of various physiological processes, consisting partly, in the transformation to its own use of material laid down in its tissues in the bud, and partly in the continuous production of fragrant vapours, which the flower gives off in that period, very often also in the production of nectar etc. If we further remember, that the considerable quantity of water which the corolla gives off to the atmosphere by transpiration, is continually replenished by fresh supplies, while the stamens on the other hand receive less water from the thalamus than they give off, it becomes clear, that the nutrition-stream moves principally in the corolla.

The consideration suggests the following questions: What means are at the disposal of the ovary for escaping the harmful consequences of too strong transpiration? Is the secretion of nectar perhaps to be regarded as one of these means?

I venture to think that I have obtained an affirmative answer to the last question and hope that I may succeed in obtaining acceptance of my opinion.

I wish to preface a description of the flower and of nectar-secretion in *Fritillaria imperialis*.

Fritillaria imperialis bears large, bell-shaped flowers turned with the opening downwards, and consisting of a perianth of two trimerous whorls, a superior ovary with a long style and tripartite stigma, and 6 long stamens, with filaments entirely enclosed in the bell, but with anthers protruding outside. Generally the style is somewhat longer, so that the stigmas are under the anthers and outside the flower. The cylindrical ovary escapes observation, as it is wholly surrounded by the fleshy filaments of the stamens, which form a close-fitting tube around it.

Not until fertilisation has taken place and the perianth has withered, do the flowers become erect; the fruits afterwards are also erect.

Each perianth-leaf bears close to its base a large saucer-shaped, shiny, white nectary, which is surrounded by an elevated border, and secretes heavy drops of fluid during the flowering-period.

The whole of the perianth is very rich in glucose, not only at the time of flowering, but already much earlier. A section through the middle of an adult perianth leaf, about half-way between base and top, shows, that the mesophyll, which is here 13—14 cells thick, consists of thin-walled cells, which leave large intercellular spaces between them. The vascular bundles are strongly developed and take up almost the whole thickness of the leaf. In no part of the transverse section can starch be detected, but the whole of the mesophyll is very rich in glucose; starch occurs only in the nectary. In a section through the nectary, 4 different parts can be made out even at low magnification. First there is the honey-secreting tissue proper, consisting of 3—4 layers of small close-fitting cells, densely filled with protoplasm and containing large nuclei. Under this there is a tissue, 8 or more cell-layers thick, composed of larger cells with very distinct intercellular spaces; these cells are crowded with numerous small starch-grains. Outwards or downwards there follows the region of the vascular bundles, where the mesophyll still contains starch. Finally the latter tissue gradually passes into that containing chromatophores, which again consists of considerably smaller cells and is closed off on the outside by an epidermis, consisting of pinacoid cells, the outer wall of which, in this region, is much thicker than in any other part of the perianth.

The starch which collects under the secretory layer, is already found in sections of very young nectaries, for instance in buds about 2.5 cm. long.

That it is from this material that nectar is afterwards formed, becomes evident on the examination of nectaries, which have already been forming honey-drops for some days; a distinct diminution of starch may then be observed, and at the end of the flowering no starch whatsoever is found.

A section through a stamen shows, that the latter is traversed by a comparatively thin vascular bundle, and that for the rest the tissue consists of large cells, which give a very strong reaction with FEHLING's test-solution for glucose. Externally the tissue is enclosed by a small-celled epidermis with a comparatively thick outer wall, which presents a granular cuticle. It may be, that by being enclosed by stamens, which are rich in glucose, the ovary is not so completely protected against the harmful consequences of exposure to the atmosphere as an inferior ovary is by the thalamus, but nevertheless the two kinds of protection are comparable; in any case the ovary thus receives considerable protection during development.

It may be of interest to note, that the stamens continue to enclose the ovary, when the anthers have fallen off. The filaments remain fresh and in their original position, as long as flowering continues.

The secretion of nectar begins soon after the perianth-leaves separate, and the tips of the anthers protrude out of the flower.

The secretion is very abundant. Generally large drops hang down from the nectaries in plants in the open. If a cut flowering specimen be placed in a glass of water, under a high bell-jar — in a fairly moist space therefore, where evaporation is limited — drops may be seen to fall down from time to time. When plants which have been grown in pots, are placed in a dark room some time before the opening of the flowers, it is found that the secretion of nectar is quite independent of light and continues day and night. If the nectar be removed by means of a pipette, the drops are renewed as well and as quickly as in the light. The nectar can be removed for several days; each time new drops appear again. From this we may deduce, that the evaporation of nectar in plants in the open air is fairly considerable, and that the nectaries continue to act as long as the flowering-period lasts.

Fritillaria imperialis is one of those plants, in which the dehiscence of the anthers depends on loss of water by transpiration. Although in many orders, such as the *Papilionaceae*, *Antirrhineae*, *Rhinanthaceae*, *Malvaceae* the dehiscence of the anthers is independent of the hygroscopic condition of the atmosphere, and the pollen is equally well liberated in a moist flower as in dry air, this is not the case in *Fritillaria*. As has been said above, the tissue of the filament indeed contains a considerable quantity of glucose, but nevertheless the osmotic action, which the sugar exerts in abstracting water from the anthers, is evidently not enough to make them dehisce. If a young flower be enclosed in a moist glass box, or a cut plant be placed under a high bell-jar in surroundings, which are only moderately damp, the anthers remain closed during the whole of the flowering period, whereas in the open air they often dehisce on the first day in bright, dry, spring weather, after having lost 90°/₀ of water. It follows from this experiment, that the anthers can dehisce, because they protrude from under the flower. If this were not the case, if the filaments were a few centimetres shorter, the moist air, inside the flower, would prevent the dehiscence of the anthers. That during the flowering-period there is a strong current of water through the vascular bundles of the perianth-leaves, which continually supplies the latter with water to compensate for the loss by transpiration, needs as little proof as the fact, that this watercurrent has been turned away from the stamens. If this were not so, there could be no question of the dehiscence of the anthers.

I now come to the conclusion, that the *Fritillaria*-flower is to be regarded as a cup in which the air is continually kept moist during the flowering period by the evaporation of 6 large drops of fluid, secreted in its upper parts by as many nectaries, the transpiration-loss of which is made good by fresh supplies of fluid, day and night, as long as flowering continues.

Inside this moist cup there are the ovary and the stamens, which remain in a state of rest during the flowering period, and receive only a small supply of water from the thalamus. For to the extent that they are enclosed in the cup (the ovary for its full length, and the stamens with the exception of the anthers) they are protected against dessication by damp surroundings, whereas the anthers, hanging out of the cup, are exposed to evaporation.

According to the analysis of BONNIER the nectar is very rich in water and contains at most 5—7 % of sugar. If there were no sugar at all in the fluid, one would not hesitate to call the nectaries of *Fritillaria* perianth-hydathodes, and to consider them quite similar to the calyx-hydathodes of *Spathodea campanulata* and similar plants.

In *Fritillaria* the nectar does not come into direct contact with the ovary, but is found outside the sexual organs. This method of nectar-secretion, which I purpose to call, for the sake of brevity, a peripheral one, is not the most general. A number of plants may indeed be cited, which agree with *Fritillaria* in this respect, such as *Trollius*, *Abutilon*, *Lilium* and *Helleborus*, but in most plants the nectar is secreted in such a way, that the ovary is directly moistened by it, as in *Labiatae*, *Boraginaceae*, *Solanaceae* and other orders. In contradistinction to the peripheral, I wish to call this a central secretion of nectar. Very often the nectar is secreted in more than one part of the flower; in such cases there is a combination of the peripheral with the central method.

In numerous plants the moistening of the ovary is greatly increased by a thick covering of soft hairs or by a thick felt, which covering is saturated with nectar in various ways. Sometimes the nectar is secreted by the ovary-wall, and ascends between the hairs, as is for instance, the case in most species of *Verbascum* and in *Helianthemum vulgare*, which are wrongly called nectarless plants. In other cases the covering itself consists of hairs which secrete glucose; this occurs for instance in the species of *Paeonia*, another genus which is wrongly considered to be devoid of nectar. Often, however, the nectar which saturates the ovary-covering, is brought up from the thalamus, as for instance in *Pulsatilla* and other *Ranunculaceae*, which will be considered below. Especially when such covered ovaries are close together (e.g. in *Pulsatilla* each flower has about 100 ovaries) it may be readily imagined, that by evaporation of the nectar the ovaries are always in a moist atmosphere. By this I mean, that one may assume, not only that the nectar is continually replenished by fresh secretion (this can indeed be observed in many plants) but also that on increased concentration, the nectar never dries up, be it, that it absorbs aqueous vapour from the air, or abstracts water from the ovary itself. This moistening of the ovary reminds us vividly of certain well-known mechanisms for protecting an organ against excessive transpiration, such as a covering of wax, or of mucilage-secreting glands. In this connexion I may point out that among plants without nectar, there are indeed some, in which the ovary is protected by wax, as in *Papaver*, *Eschscholtzia*, and *Glaucium* or by mucilage, as in species of *Lysimachia*, *Ononis spinosa*, and *Verbascum Blattaria*. It thus becomes intelligible, that these plants can do without nectar. In *Verbascum Blattaria* the ovary, which is fairly deeply hidden, is covered from top to bottom with compound glands, which correspond in structure with lupulin- and *Ribes* glands, continually pouring out a layer of mucilage over the ovary.

This is the more remarkable and important, since, as was mentioned above, the ovary of all other *Verbascum*-species is covered with a felt, rich in glucose. We find therefore in different species of the same genus two different means of protection, to which the same biological significance must be attached.

I now wish to explain further, by some notes on *Ranunculaceae* and *Malvaceae*, what was said above with reference to the secretion of nectar in different parts of the flower.

Let us consider first of all the flower of *Trollius europaeus* L.

In *Trollius* the 11 or 13 large, hemispherical sepals with overlapping edges, form an approximately ball-shaped envelope round the sexual organs. The petals, generally 10 in number, are yellow and spatulate, and secrete honey on the middle of their inner surfaces. The stamens numbering about 160 and placed in numerous whorls, surround about 30 ovaries. Except for a small opening, facing upwards, the flowers are closed ; only the stigmas come wholly or partially into view.

At the beginning of the flowering period the anthers are at about the same height as the stigmas, and the ovaries are surrounded and protected by the column of stamens.

Later this is not the case to the same extent, although a few whorls of the inner stamens, the anthers of which do not come to complete development, retain their places.

As in *Fritillaria*, the ovaries of *Trollius* are in a moist space, and are furthermore protected laterally by the stamens. Whereas, however, the humidity of the flower in *Fritillaria* does not interfere with the dehiscence of the anthers, because these are outside the flower, this is not so in *Trollius*, where the dehiscence of the anthers is equally dependent on the evaporation of superfluous water into the air, for in *Trollius* the stamens are enclosed within the calyx.

This is the explanation of the remarkable phenomenon, that the stamens, beginning with those of the outer whorl and then gradually from the periphery to the centre, become elongated soon after the opening of the flower and bend inwards, until their anthers are near the opening; the anthers of the inner staminal whorl then come to lie immediately above the stigmas. If one places a young flower in a closed glass box, the phenomenon may be followed step by step, and one observes at the same time, that as long as the flower remains in the glass box, the anthers remain closed. In an open box on the other hand, the anthers are seen to dehisce as soon as they have come under the opening of the flower, and their pollen is seen to be scattered on the stigmas. Observation in the field likewise proves, that the anthers remain closed in damp weather.

Honey is not secreted in any place other than the petals. In the main the arrangement of the flower is quite like that of *Fritillaria*. The closed condition of the corolla can hardly be explained otherwise than as a device to prevent the rapid evaporation of the nectar into the air and is connected with the erect position of the flower [1]).

As a second example of the methods of nectar-secretion in *Ranunculaceae*, I now choose the flowers of *Clematis* and of *Anemone*, which do not possess petals, but where the calyx takes the place of the corolla, and where no nectar is observed on the periphery of the flower. This is the reason, why they are referred to as nectarless plants in the literature on the biology of the flower. That this is by no means correct, is at once evident when we wash the ovaries, which are thickly covered with silky hairs, for a moment with a drop of distilled water on a slide, and then warm the water with a drop of Fehling's solution; we then obtain a strong glucose-reaction, proving that the hairy covering of the ovary is saturated with nectar. Further investigation shows, that this nectar is derived from the interstaminal portion of the thalamus.

The droplets of nectar, which are secreted here, are sucked up between the stamens and the ovaries and are retained, especially by the hairy covering of the latter.

I must now recall that many years ago, Bonnier already drew attention to the interstaminal secretion of nectar in *Anemone nemorosa*. He stated that the thalamus contains much sugar, and that its interstaminal portion is covered with numerous thin walled papillae, from which, under favourable conditions, minute drops of nectar are seen to exude. My own investigations have shown me that what Bonnier [1]) observed, may be called a pretty general phenomenon in the order of *Ranunculaceae* i.e. in many genera, nectar is secreted from this portion of the thalamus.

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[1]) I believe that this is also the explanation of the closed flowers of *Calceolaria*, *Fumariaceae*, *Antirrhineae*, *Rhinanthaceae* etc.

The flowers of *Anemone* and of *Clematis* may therefore be contrasted with those of *Trollius*, as regards secretion of nectar. Here the nectar comes into direct contact with the ovaries and it is evident, that the numerous drops of honey, which are found everywhere between the stamens, and which are constantly renewed, contribute not a little to the maintenance of a certain degree of humidity in the neighbourhood of the ovaries.

It is remarkable, that in many other *Ranunculaceae* the nectar is secreted in the flower in two places, so that a peripheral and a central secretion may be distinguished. It should be noted, that in some genera the two methods of secretion are of about equal importance to the plant, but that in other genera the peripheral one is much the least important.

The flower of *Aconitum* may serve as an example of a plant in which both secretions are of importance for the protection of the sexual organs.

At the beginning of the flowering-period the 3—5 quite glabrous ovaries have not yet reached their full development. They can scarcely be discerned, as they are enclosed by the numerous stamens. These stamens are distinguished by broad filaments, which are very rich in glucose, and which, being closely pressed against the ovaries, protect the latter against external influences. The sexual organs are kept moist by a secretion of nectar from the interstaminal portion of the thalamus. [2]) The sepals and petals are also rich in glucose.

The two superior petals are metamorphosed to nectaries with long stalks and during the time of flowering these secrete a copious supply of honey. The two superior, dark blue sepals have coalesced to form a helmet-shaped hood, which, as long as the flower is still in bud, encloses it for the most part and further, during the flowering-period, acts as a protective roof to the two nectaries and the sexual organs below them, while the latter are surrounded by the remaining sepals and petals. The secretion of nectar has once more rendered the flower a moist chamber, in which the sexual organs are protected against the dangers of dessication. At first the stamens, with anthers bent downwards and closed, lie turned away from the entrance of the moist chamber. Later they become erect; afterwards they become elongated, and so bring the anthers to the entrance of the flower, where they can give up their excess of moisture to the air, at least when the latter is not too damp. As they dehisce, the stamens again bend downwards with empty anthers. The broadened parts of the filaments do not, however, bend in this way, but retain their original position and protect the ovaries throughout the whole of the flowering period. It is not until this stage that the stigmas, which are now fully developed, come to the entrance of the flower.

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[1]) Bonnier, G,. Les nectaires. Annales des sciences naturelles. Botanique. Tome VIII. 1879. p. 141.

[2]) Not unfrequently the nectar-drops can be detected on the stamens with a simple lens; the presence of nectar between the stamens may moreover be easily demonstrated chemically, by depriving a young flower of its calyx and corolla, and washing it with water.

Although the corollar-nectaries of *Aconitum* are not much less important than the thalamus, as regards secretion of nectar, this is not so in all genera of *Ranunculaceae*, as has already been pointed out. In *Ranunculus*, *Batrachium*, and *Ficaria* the corollar-secretion is of much less significance and that of the thalamus certainly much more important. In *Pulsatilla* the corollar-secretion is still further reduced and in the genera *Paeonia*, *Caltha*, *Anemone*, and *Clematis* the corollar-nectaries no longer occur; here the honey-secretion of the thalamus has become of primary importance.

In *Caltha palustris* secretion of nectar can be observed in the flower in three places: first at the periphery of the thalamus, where in the allied *Helleboreae* the stalked corollar-nectaries are placed; secondly at the interstaminal part of the thalamus; thirdly on the wall of each ovary. The ovaries of *Caltha* are glabrous, but on both sides of each ovary there is a spot, covered by hundreds of delicate papillae with very thin walls. Each of the latter secretes a minute droplet of nectar, and the large drop, which is formed by the fusion of the droplets, can easily be detected with a lens between any two adjacent ovaries. The parietal papillae here replace the hairs of other genera.

The extent of the reduction in the peripheral nectar-secretion of other genera is best observed in *Ranunculus* and in *Pulsatilla*.

The flower of *Ranunculus acer* for instance, agrees with that of *Trollius* both as regards the position of the stamens relative to the ovaries and the elongation and inward-movement of the stamens. The nectar-secretion at the base of the petals cannot contribute to the protection of the sexual organs by keeping the flower moist, except possibly on the first day of flowering, when the corolla is still cup-shaped. In no case can this secretion be of importance during subsequent stages, when the corolla is spread out. If there were here no nectar-secretion at the interstaminal portion of the thalamus, the ovaries would be in danger of rapid destruction owing to dessication.

In *Ranunculus auricomus* the peripheral secretion is still much less important. Here often one or two and sometimes all petals are wanting, and with them the nectaries; frequently, moreover, the nectaries are rudimentary.

In the genus *Pulsatilla* the peripheral nectar-secretion is likewise insignificant (its seat is in the metamorphosed anthers of the outer whorl). In *Pulsatilla vulgaris, P. pratensis* and *P. vernalis* it has been observed, that the nectaries frequently do not secrete any nectar; here nectar-containing and nectarless plants are found; *P. alpina* is quite free from nectar, according to SCHULZ. The nectar-secretion from the thalamus is therefore, also in this genus, of primary importance; during the flowering period the numerous ovaries are each, as it were, covered by a mantle saturated with glucose.

In the natural order of *Malvaceae* the true significance of nectar-secretion is not less clear than among *Ranunculaceae*.

I shall not be able to consider this subject in detail in the present communication, but may recall, that BEHRENS showed in 1879, that in *Abutilon, Althaea*, and *Malva* the bottom of the calyx bears a nectary, consisting of a large number of closely crowded multicellular "Sekretions-Papillen", which together form a large secreting surface. Each "Papille" consists of a large number of cells, placed in a row, e. g. in *Abutilon insigne* 12—14. What BEHRENS thus describes probably applies, as far as my own investigation extends, to all *Malvaceae*. I found these nectaries also in the genera *Hibiscus, Kitaibelia, Malope, Anoda* and *Sidalcea*.

Whether in general, however, secretion is a constant phenomenon in these calyx-nectaries, is doubted by various authors. Of many species it is not known whether they ever contain nectar, and of other species the accounts are contradictory; in the case of some, it might be assumed, that the individuals of the same species differ among themselves. Thus, for instance, KIRCHNER could not find any nectaries in *Abutilon Avicennae*, whereas in this country the same plant is so rich in nectar, that the latter can be seen with the naked eye. As regards *Hibiscus*, those species, which are best known in Europe, namely *H. syriacus, H. Trionum*, and *H. esculentus* are regarded as nectarless. The large flowers of *Abutilon* are however very rich in nectar, so much so, that the nectar is removed by honey-birds.

Being peripheral, the secretion of the calyx-nectaries may be compared with that of the corollar-nectaries of *Ranunculaceae*. My investigations have now shown me, that in the order of *Malvaceae* a central secretion of nectar may also be observed, which in most genera gives the impression of being the more important — perhaps in all genera except *Abutilon*.

As is well known, the stamens in *Malvaceae* are united to form a tube. This staminal cylinder, which extends upwards round the ovary, is, at its base, joined to the corolla in such a way that their common tissue encloses the ovary and hides it from view. If the ovary be now liberated from its little "house", its wall, in almost all *Malvaceae*, is found to be thickly covered with nectar-secreting trichomes of the same structure as those, which constitute the calyx-nectary (Sekretionspapillen of BEHRENS) and these trichomes continually pour a layer of glucose on the ovary. In *Hibiscus esculentus* and in *H. Trionum* these ovarial trichomes are even larger than those of the calyx-nectary, and consist of 28 cells. The ovaries are therefore not only enclosed in the staminal tube, but are always confined in a space, kept moist by nectar-secretion.

I hope afterwards to return to a detailed study of this order, which is so extremely interesting as regards nectar-production.

Before closing this communication, I still wish to call attention to two important matters. In the first place to the secretion, which takes place in many flowers, while they are still in bud. We are accustomed to assume, that secretion only begins at or after the opening of the flower, but I have found many exceptions to this rule. The phenomenon may be observed in *Ranunculaceae* especially. The ovaries of *Clematis Viticella*, covered with silken hairs, the ovaries of *Paeonia*, *Pulsatilla* and of *Aconitum* are bathed in nectar, long before the opening of the bud, and it may probably be assumed with safety, that the secretion of nectar, which already takes place in the bud, serves here to protect the sexual organs, and is therefore comparable to the secretion of water in flowers with a water-calyx. In the flowers of *Aconitum* I found that indeed the central, but not the peripheral, secretion may be observed before the opening; this suggested to me that the latter secretion serves more especially to keep the flower moist during the flowering period. Further investigation will be required to show, whether this difference can also be traced in other plants with a double secretion of nectar.

Before there is any question of the flower's opening, a copious secretion of nectar may also be observed in other plants, such as *Melandrium album* (*Lychnis vespertina*), *Hyoscyamus niger*, *Galanthus nivalis*, many *Papilionaceae* and *Epilobium angustifolium.*

In the second place I think it may be useful to refer briefly to the so-called nectarless plants, because it might be argued that these do not support the truth or general validity of the hypothesis, put forward above.

I have already had an opportunity of pointing out, that some plants, which do not contain nectar, have their ovarian-wall covered with *wax*, and others with *glands secreting mucilage*; to these secretions the same biological significance is attached as that, which I think should be attributed to nectar-secretion. Furthermore, I have already mentioned a number of plants, which are recorded as nectarless, but which, nevertheless, must certainly be reckoned among those containing nectar, namely species of *Anemone*, *Clematis*, *Pulsatilla*, and *Paeonia* in the order of *Ranunculaceae*, also *Helianthemum vulgare* and the various species of *Verbascum* and *Hibiscus.* I will only add, that it can be easily shown by chemical means, that the so-called nectarless *Rosaceae*: *Rosa*, *Poterium*, *Agrimonia*, *Aruncus* and *Spiraea* have been wrongly included in this class. Here indeed the nectar is often difficult to observe, but it is none the less present, as in other *Rosaceae*. If the flowers are extracted with water, so that the nectar, which has been thickened by evaporation, passes into solution, the presence of glucose may readily be demonstrated in all these plants. Finally it may be pointed out in this connexion, that very many plants do not require a special protection by nectar, either because the ovary continues its growth without interruption, (on account of early fertilisation, which often already takes place in the bud) or because it is not exposed to the air during the flowering period.

The latter case occurs especially in the genera *Plantago* and *Luzula*, in *Nymphaea alba* and *Erythraea Centaureum*, in *Iuncus*, in most Grasses and in other anemophilous plants.

Mathematics. — "*On a theorem of* PAINLEVÉ's." By Prof. W. KAPTEYN.

1. PAINLEVÉ, in his well-known memoirs on differential equations of the first order, investigated the question when the integrals possess a definite number of values or branches if the independent variable turns round the critical parametric (not the fixed) points.

For differential equations of the first degree

$$\frac{dy}{dx}=\frac{P(x,y)}{Q(x,y)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where P and Q represent polynomials in y, he has proved that if the integrals possess n branches, there always exists a substitution

$$u = \frac{y^n + L_{n-1}\,y^{n-1} + \ldots + L_1 y}{M_{n-1}\,y^{n-1} + \ldots + M_1\,y + 1} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

by which the equation (1) may be reduced to an equation of RICCATI

$$\frac{du}{dx} = Gu^2 + Hu + K. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

the coefficients L, M, G, H, K being functions of x.

Our object in this paper is to prove this proposition in another way, starting from the form of the integral

$$C = \frac{\lambda_n\,y^n + \lambda_{n-1}\,y^{n-1} + \ldots + \lambda_1\,y + \lambda_0}{y^n + \mu_{n-1}\,y^{n-1} + \ldots + \mu_1\,y + \mu_0} \quad . \quad . \quad . \quad (4)$$

where C represents an arbitrary constant and λ and μ functions of x. The treatment of the two cases $n = 2$ and $n = 3$ will be sufficient to show that the proposition holds good generally.

2. If $n = 2$, it is evident from the integral

$$C = \frac{\lambda_2 y^2 + \lambda_1 y + \lambda_0}{y^2 + \mu_1 y + \mu_0} = const. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

that the differential equation must be of the form

$$\frac{dy}{dx} = \frac{a_4 y^4 + a_3 y^3 + a_2 y^2 + a_1 y + a_0}{b_2 y^2 + 2b_1 y + b_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

the coefficients a and b representing functions of x.

Differentiating the equation (5), we find between a, b, λ, μ, the following relations θ being an indefinite factor,

$$\left.\begin{aligned}
\theta a_4 &= \lambda_2' \\
\theta a_3 &= \mu_1\lambda_2' + \lambda_1' - \lambda_2\mu_1' \\
\theta a_2 &= \mu_0\lambda_2' + \mu_1\lambda_1' + \lambda_0' - \lambda_1\mu_1' - \lambda_2\mu_0' \\
\theta a_1 &= \mu_0\lambda_1' + \mu_1\lambda_0' - \lambda_0\mu_1' - \lambda_1\mu_0' \\
\theta a_0 &= \mu_0\lambda_0' - \lambda_0\mu_0' \\
\theta b_2 &= \lambda_1 - \mu_1\lambda_2 \\
\theta b_1 &= \lambda_0 - \mu_0\lambda_2 \\
\theta b_0 &= \mu_1\lambda_0 - \mu_0\lambda_1.
\end{aligned}\right\} \quad . \quad . \quad . \quad (7)$$

From the three latter equations (7) may be induced

$$\left.\begin{array}{r} b_0\lambda_2 - b_1\lambda_1 + b_2\lambda_0 = 0 \\ b_1\mu_1 - b_2\mu_0 - b_0 = 0 \end{array}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

and from the five preceding

$$\mu_0' = \theta \begin{vmatrix} a_4 & 1 & 0 & 0 & 0 \\ a_3 & \mu_1 & 1 & 0 & -\lambda_2 \\ a_2 & \mu_0 & \mu_1 & 1 & -\lambda_1 \\ a_1 & 0 & \mu_0 & \mu_1 & -\lambda_0 \\ a_0 & 0 & 0 & \mu_0 & 0 \end{vmatrix} : \begin{vmatrix} 1 & 0 & 0 & 0 & 0 \\ \mu_1 & 1 & 0 & -\lambda_2 & 0 \\ \mu_0 & \mu_1 & 1 & -\lambda_1 & -\lambda_2 \\ 0 & \mu_0 & \mu_1 & -\lambda_0 & -\lambda_1 \\ 0 & 0 & \mu_0 & 0 & -\lambda_0 \end{vmatrix} .$$

This equation may be easily reduced to an equation of RICCATI. For adding up, in the first determinant the third column multiplied by λ_2 to the fifth and in the second determinant the second and third columns each multiplied by λ_2 to the fourth and last, we get

$$\mu_0' = - \begin{vmatrix} a_4 & 1 & 0 & 0 & 0 \\ a_3 & \mu_1 & 1 & 0 & 0 \\ a_2 & \mu_0 & \mu_1 & 1 & b_2 \\ a_1 & 0 & \mu_0 & \mu_1 & b_1 \\ a_0 & 0 & 0 & \mu_0 & 0 \end{vmatrix} : \begin{vmatrix} 1 & 0 & 0 & 0 & 0 \\ \mu_1 & 1 & 0 & 0 & 0 \\ \mu_0 & \mu_1 & 1 & b_2 & 0 \\ 0 & \mu_0 & \mu_1 & b_1 & b_2 \\ 0 & 0 & \mu_0 & 0 & b_1 \end{vmatrix} .$$

If now we substitute

$$\mu_1 = \frac{b_0 + b_2\mu_0}{b_1} .$$

in the denominator, and subtract the fourth and fifth columns each multiplied by $\frac{\mu_0}{b_1}$ from the second and third, we find

$$\begin{vmatrix} 1 & 0 & 0 & 0 & 0 \\ \mu_1 & 1 & 0 & 0 & 0 \\ \mu_0 & \frac{b_0}{b_1} & 1 & b_2 & 0 \\ 0 & 0 & \frac{b_0}{b_1} & b_1 & b_2 \\ 0 & 0 & 0 & 0 & b_1 \end{vmatrix} = b_1^2 - b_0 b_2$$

If we in the same way subtract the fifth column multiplied by $\frac{\mu_0}{b_1}$ from the third, the numerator takes the form

$$\begin{vmatrix} a_4 & 1 & 0 & 0 & 0 \\ a_3 & \dfrac{b_0+b_2\mu_0}{b_1} & 1 & 0 & 0 \\ a_2 & \mu_0 & \dfrac{b_0}{b_1} & 1 & b_2 \\ a_1 & 0 & 0 & \dfrac{b_0+b_2\mu_0}{b_1} & b_1 \\ a_0 & 0 & 0 & \mu_0 & 0 \end{vmatrix} = A\,\mu_0^2 + B\mu_0 + C$$

where the coefficients have to be determined still.

If we put $\mu_0 = 0$, the coefficient C is found to be

$$C = a_0 \begin{vmatrix} 1 & b_2 \\ \dfrac{b_0}{b_1} & b_1 \end{vmatrix} = \frac{a_0}{b_1}(b_1^2 - b_0 b_2).$$

Dividing further both members by μ_0^2 and supposing afterwards $\mu_0 = \infty$, we get

$$A = \begin{vmatrix} a_4 & 0 & 0 & 0 & 0 \\ a_3 & \dfrac{b_2}{b_1} & 1 & 0 & 0 \\ a_2 & 1 & \dfrac{b_0}{b_1} & 1 & b_2 \\ a_1 & 0 & 0 & \dfrac{b_2}{b_1} & b_1 \\ a_0 & 0 & 0 & 1 & 1 \end{vmatrix} = -\,a_4 b_1 \begin{vmatrix} \dfrac{b_2}{b_1} & 1 \\ 1 & \dfrac{b_0}{b_1} \end{vmatrix} = \frac{a_4}{b_1}\,(b_1^2 - b_0 b_2).$$

Differentiating both members with respect to μ_0, and substituting $\mu_0 = 0$, we get for B the form

$$B = \begin{vmatrix} a_4 & 0 & 0 & 0 & 0 \\ a_3 & \dfrac{b_2}{b_1} & 1 & 0 & 0 \\ a_2 & 1 & \dfrac{b_0}{b_1} & 1 & b_2 \\ a_1 & 0 & 0 & \dfrac{b_0}{b_1} & b_1 \\ a_0 & 0 & 0 & 0 & 0 \end{vmatrix} + \begin{vmatrix} a_4 & 1 & 0 & 0 & 0 \\ a_3 & \dfrac{b_0}{b_1} & 1 & 0 & 0 \\ a_2 & 0 & \dfrac{b_0}{b_1} & 0 & b_2 \\ a_1 & 0 & 0 & \dfrac{b_2}{b_1} & b_1 \\ a_0 & 0 & 0 & 1 & 0 \end{vmatrix}.$$

The first of these determinants is identically zero; the second developed, gives

$$B = -\frac{b_0^2}{b_1}a_4 + b_0a_3 - b_1a_2 + b_2a_1 - \frac{b_2^2}{b_1}a_0.$$

Hence μ_0 satisfies the following equation of RICCATI

$$\mu_0' = -\frac{a_4}{b_1}(b_1^2 - b_0b_2)\mu_0^2 + \frac{1}{b_1}(b_0^2a_4 - b_0b_1a_3 + b_1^2a_2 - b_1b_2a_1 + b_2^2a_0)\mu_0 -$$

$$-\frac{a_0}{b_1}(b_1^2 - b_0b_2). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

We now proceed to find the substitution of PAINLEVÉ.

From the general integral

$$C = \frac{\lambda_2y^2 + \lambda_1y + \lambda_0}{y^2 + \mu_1y + \mu_0}$$

it is evident that μ_0 is that particular solution of the equation (9) which satisfies the equation

$$y^2 + \frac{b_0 + b_2\mu_0}{b_1}y + \mu_0 = 0$$

if we attribute to y that particular integral of (6) which corresponds to the value $C = \infty$.

Therefore

$$\mu_0 = -\frac{b_1y^2 + b_0y}{b_2y + b_1}$$

is the substitution which reduces the differential equation (6) to (9).

3. From the preceding we may also deduce the conditions which must be satisfied by the given differential equation. For the three last equations (7) give

$$\frac{d}{dx}\left(\frac{b_2}{b_1}\right) = \frac{d}{dx}\ \frac{\lambda_1 - \mu_1\lambda_2}{\lambda_0 - \mu_0\lambda_2} \text{ and } \frac{d}{dx}\left(\frac{b_0}{b_1}\right) = \frac{d}{dx}\ \frac{\mu_1\lambda_0 - \mu_0\lambda_1}{\lambda_0 - \mu_0\lambda_2}$$

or

$$\theta(b_1b_2' - b_2b_1') = -b_0\lambda_2' + b_1\lambda_1' - b_2\lambda_0' - b_1\lambda_2\mu_1' + b_2\lambda_2\mu_0'$$

and

$$\theta(b_1b_0' - b_0b_1') = b_0\mu_0\lambda_2' - b_1\mu_0\lambda_1' + b_2\mu_0\lambda_0' + b_1\lambda_0\mu_1' - b_2\lambda_0\mu_0'.$$

Combining each of these with the five first equations (7) and eliminating λ_2' λ_1' λ_0' μ_1' μ_0' we may write the conditions

$$\begin{vmatrix} a_4 & 1 & 0 & 0 & 0 & 0 \\ a_3 & \mu_1 & 1 & 0 & -\lambda_2 & 0 \\ a_2 & \mu_0 & \mu_1 & 1 & -\lambda_1 & -\lambda_2 \\ a_1 & 0 & \mu_0 & \mu_1 & -\lambda_0 & -\lambda_1 \\ a_0 & 0 & 0 & \mu_0 & 0 & -\lambda_0 \\ (b_1b_2') & -b_0 & b_1 & -b_2 & -b_1\lambda_2 & b_2\lambda_2 \end{vmatrix} = 0$$

and
$$\begin{vmatrix} a_4 & 1 & 0 & 0 & 0 & 0 \\ a_3 & \mu_1 & 1 & 0 & -\lambda_2 & 0 \\ a_2 & \mu_0 & \mu_1 & 1 & -\lambda_1 & -\lambda_2 \\ a_1 & 0 & \mu_0 & \mu_1 & -\lambda_0 & -\lambda_1 \\ a_0 & 0 & 0 & \mu_0 & 0 & -\lambda_0 \\ (b_1b_0') & b_0\mu_0 & -b_1\mu_0 & b_2\mu_0 & b_1\lambda_0 & -b_2\lambda_0 \end{vmatrix} = 0$$

where (b_1b_2') and (b_1b_0') mean $b_1b_2' - b_2b_1'$ and $b_1b_0' - b_0b_1'$ respectively.

Reducing these determinants in the same way as before, we have immediately

$$\begin{vmatrix} a_4 & 1 & 0 & 0 & 0 & 0 \\ a_3 & \mu_1 & 1 & 0 & 0 & 0 \\ a_2 & \mu_0 & \frac{b_0}{b_1} & 1 & b_2 & 0 \\ a_1 & 0 & 0 & \frac{b_0}{b_2} & b_1 & b_2 \\ a_0 & 0 & 0 & 0 & 0 & b_1 \\ \alpha & \beta & \gamma & \delta & \varepsilon & \zeta \end{vmatrix} = 0 \quad . \; . \; . \; . \; . \; . \quad (10)$$

the latter row representing the following values

$$\left.\begin{array}{llllll} \alpha = (b_1b_2') & \beta = -b_0 & \gamma = b_1 & \delta = -b_2 & \varepsilon = 0 & \zeta = 0 \\ \alpha = (b_1b_0') & \beta = b_0\mu_0 & \gamma = 0 & \delta = 0 & \varepsilon = -b_1^2 & \zeta = b_1b_2 \end{array}\right\} \quad . \quad . \quad (11)$$

If we write $\mu_1 = \frac{b_0 + b_2\mu_0}{b_1}$ the determinant (10) takes the form $A\mu_0 + B$. By differentiation with respect to μ_0, A is determined by

$$A = -a_4b_1 \begin{vmatrix} \frac{d\beta}{d\mu_0} & \gamma & \delta & \varepsilon \\ \frac{b_2}{b_1} & 1 & 0 & 0 \\ 1 & \frac{b_0}{b_1} & 1 & b_2 \\ 0 & 0 & \frac{b_0}{b_1} & b_1 \end{vmatrix}$$

or

$$A = -a_4\, b_1\, (b_1^2 - b_0\, b_2) \left[\frac{1}{b_1} \frac{d\beta}{d\mu_0} - \frac{b_2}{b_1^2}\gamma - \frac{1}{b_1}\delta + \frac{b_0}{b_1^2}\varepsilon \right].$$

In both cases this expression vanishes. Therefore both conditions are found by writing $\mu_0 = 0$ in the equation (10). In this way the conditions we looked for, are the following

$$\left| \begin{array}{cccccc} a_4 & 1 & 0 & 0 & 0 & 0 \\ a_3 & \frac{b_0}{b_1} & 1 & 0 & 0 & 0 \\ a_2 & 0 & \frac{b_0}{b_1} & 1 & b_2 & 0 \\ a_1 & 0 & 0 & \frac{b_0}{b_1} & b_1 & b_2 \\ a_0 & 0 & 0 & 0 & 0 & b_1 \\ \alpha & (\beta)_{\mu_0=0} & \gamma & \delta & \varepsilon & \zeta \end{array} \right| = 0 \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where the last row is given by the relations (11).

4. When $n = 3$, the general integral

$$C = \frac{\lambda_3 y^3 + \lambda_2 y^2 + \lambda_1 y + \lambda_0}{y^3 + \mu_2 y^2 + \mu_1 y + \lambda_0} = \text{const.}$$

shows, that the differential equation must be of the form

$$\frac{dy}{dx} = \frac{a_6 y^6 + a_5 y^5 + a_4 y^4 + a_3 y^3 + a_2 y^2 + a_1 y + a_0}{b_4 y^4 + 4 b_3 y^3 + 6 b_2 y^2 + 4 b_1 y + b_0} \quad . \quad . \quad (14)$$

with the following relations between the coefficients a, b, λ, μ:

$$\left. \begin{aligned} \theta a_6 &= \lambda_3' \\ \theta a_5 &= \mu_2 \lambda_3' + \lambda_2' - \lambda_3 \mu_2' \\ \theta a_4 &= \mu_1 \lambda_3' + \mu_2 \lambda_2' + \lambda_1' - \lambda_2 \mu_2' - \lambda_3 \mu_1' \\ \theta a_3 &= \mu_0 \lambda_3' + \mu_1 \lambda_2' + \mu_2 \lambda_1' + \lambda_0' - \lambda_1 \mu_2' - \lambda_2 \mu_1' - \lambda_3 \mu_0' \\ \theta a_2 &= \mu_0 \lambda_2' + \mu_1 \lambda_1' + \mu_2 \lambda_0' - \lambda_0 \mu_2' - \lambda_1 \mu_1' - \lambda_2 \mu_0' \\ \theta a_1 &= \mu_0 \lambda_1' + \mu_1 \lambda_0' - \lambda_0 \mu_1' - \lambda_1 \mu_0' \\ \theta a_0 &= \mu_0 \lambda_0' - \lambda_0 \mu_0' \\ \theta b_4 &= \lambda_2 - \lambda_3 \mu_2 \\ 4\theta b_3 &= 2\lambda_1 - 2\lambda_3 \mu_1 \\ 6\theta b_2 &= 3\lambda_0 + \lambda_1 \mu_2 - \lambda_2 \mu_1 - 3\lambda_3 \mu_0 \\ 4\theta b_1 &= 2\lambda_0 \mu_2 - 2\lambda_2 \mu_0 \\ \theta b_0 &= \lambda_0 \mu_1 - \lambda_1 \mu_0 \end{aligned} \right\} \quad (15)$$

Eliminating alternately the μ's and λ's from the five last equations (15) we have

$$\left.\begin{array}{l}
3b_0\lambda_3^2 - 6b_2\lambda_1\lambda_3 + 2b_3(\lambda_1\lambda_2 + 3\lambda_0\lambda_3) - b_4\lambda_1^2 = 0 \\
6b_1\lambda_3^2 - 6b_2\lambda_2\lambda_3 + 2b_3\lambda_2^2 + b_4(3\lambda_0\lambda_3 - \lambda_1\lambda_2) = 0 \\
(3\mu_0 - \mu_1\mu_2)b_4 + 2\mu_2^2 b_3 - 6\mu_2 b_2 + 6b_1 = 0 \\
\mu_1^2 b_4 - 2(3\mu_0 + \mu_1\mu_2)b_3 + 6\mu_1 b_2 - 3b_0 = 0
\end{array}\right\} \quad . \quad . \quad (16)$$

The two latter equations (16) enable us to express μ_2 and μ_1 in function of μ_0. For multiplying the first of these by $2b_3$, the second by b_4, and adding up, we find the following quadratic equation

$$(\mu_1 b_4 - 2\mu_2 b_3)^2 + 6b_2(\mu_1 b_4 - 2\mu_2 b_3) + 3(4b_1 b_3 - b_0 b_4) = 0$$

so

$$\mu_1 b_4 - 2\mu_2 b_3 = -3b_2 + \sqrt{3i_2}$$

where the square root stands for both values, and i_2 represents the expression

$$i_2 = 3b_2^2 - 4b_1 b_3 + b_0 b_4.$$

This result, in connexion with

$$\mu_1(\mu_1 b_4 - 2\mu_2 b_3 + 6b_2) = 3b_0 + 6\mu_0 b_3$$

gives

$$\mu_1 = \frac{3b_0 + 6\mu_0 b_3}{3b_2 + \sqrt{3i_2}} \qquad \mu_2 = \frac{6b_1 + 3\mu_0 b_4}{3b_2 + \sqrt{3i_2}}.$$

Now the first seven equations (15) lead up to

$$\mu_0' = \theta \begin{vmatrix}
a_6 & 1 & 0 & 0 & 0 & 0 & 0 \\
a_5 & \mu_2 & 1 & 0 & 0 & -\lambda_3 & 0 \\
a_4 & \mu_1 & \mu_2 & 1 & 0 & -\lambda_2 & -\lambda_3 \\
a_3 & \mu_0 & \mu_1 & \mu_2 & 1 & -\lambda_1 & -\lambda_2 \\
a_2 & 0 & \mu_0 & \mu_1 & \mu_2 & -\lambda_0 & -\lambda_1 \\
a_1 & 0 & 0 & \mu_0 & \mu_1 & 0 & -\lambda_0 \\
a_0 & 0 & 0 & 0 & \mu_0 & 0 & 0
\end{vmatrix} : \begin{vmatrix}
1 & 0 & 0 & 0 & 0 & 0 & 0 \\
\mu_2 & 1 & 0 & 0 & -\lambda_3 & 0 & 0 \\
\mu_1 & \mu_2 & 1 & 0 & -\lambda_2 & -\lambda_3 & 0 \\
\mu_0 & \mu_1 & \mu_2 & 1 & -\lambda_1 & -\lambda_2 & -\lambda_3 \\
0 & \mu_0 & \mu_1 & \mu_2 & -\lambda_0 & -\lambda_1 & -\lambda_2 \\
0 & 0 & \mu_0 & \mu_1 & 0 & -\lambda_0 & -\lambda_1 \\
0 & 0 & 0 & \mu_0 & 0 & 0 & -\lambda_0
\end{vmatrix}$$

which reduces to an equation of RICCATI. For adding up in the numerator λ_3 times the third column to the sixth and λ_3 times the fourth to the seventh, and in the denominator λ_3 times the second, the third, and the fourth columns respectively to the fifth, sixth, and seventh, we find

$$\mu_0' = -\begin{vmatrix} a_6 & 1 & 0 & 0 & 0 & 0 & 0 \\ a_5 & \mu_2 & 1 & 0 & 0 & 0 & 0 \\ a_4 & \mu_1 & \mu_2 & 1 & 0 & b_4 & 0 \\ a_3 & \mu_0 & \mu_1 & \mu_2 & 1 & 2b_3 & b_4 \\ a_2 & 0 & \mu_0 & \mu_1 & \mu_2 & u & 2b_3 \\ a_1 & 0 & 0 & \mu_0 & \mu_1 & 0 & u \\ a_0 & 0 & 0 & 0 & \mu_0 & 0 & 0 \end{vmatrix} : \begin{vmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ \mu_2 & 1 & 0 & 0 & 0 & 0 & 0 \\ \mu_1 & \mu_2 & 1 & 0 & b_4 & 0 & 0 \\ \mu_0 & \mu_1 & \mu_2 & 1 & 2b_3 & b_4 & 0 \\ 0 & \mu_0 & \mu_1 & \mu_2 & u & 2b_3 & b_4 \\ 0 & 0 & \mu_0 & \mu_1 & 0 & u & 2b_3 \\ 0 & 0 & 0 & \mu_0 & 0 & 0 & u \end{vmatrix}$$

where u is determined by the relation

$$\theta u = \frac{6\theta b_2 + \lambda_1\mu_2 - \lambda_2\mu_1}{3} = \theta\,\frac{6b_2 + \mu_1 b_4 - 2\mu_2 b_3}{3} = \frac{\theta}{3}(3b_2 + \sqrt{3i_2}) = \frac{\theta}{3}\,m.$$

If we substract in the numerator $\frac{3\mu_0}{m}$ times the sixth and seventh columns from the third and fourth and in the denominator $\frac{3\mu_0}{m}$ times the fifth, sixth, and seventh from the second, third and fourth columns, the value of μ'_0 reduces to

$$\mu_0' = -\begin{vmatrix} a_6 & 1 & 0 & 0 & 0 & 0 & 0 \\ a_5 & \mu_2 & 1 & 0 & 0 & 0 & 0 \\ a_4 & \mu_1 & \frac{6b_1}{m} & 1 & 0 & b_4 & 0 \\ a_3 & \mu_0 & \frac{3b_0}{m} & \frac{6b_1}{m} & 1 & 2b_3 & b_4 \\ a_2 & 0 & 0 & \frac{3b_0}{m} & \mu_2 & \frac{m}{3} & 2b_3 \\ a_1 & 0 & 0 & 0 & \mu_1 & 0 & \frac{m}{3} \\ a_0 & 0 & 0 & 0 & \mu_0 & 0 & 0 \end{vmatrix} : \begin{vmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ \mu_2 & 1 & 0 & 0 & 0 & 0 & 0 \\ \mu_1 & \frac{6b_1}{m} & 1 & 0 & b_4 & 0 & 0 \\ \mu_0 & \frac{3b_0}{m} & \frac{6b_1}{m} & 1 & 2b_3 & b_4 & 0 \\ 0 & 0 & \frac{3b_0}{m} & \frac{6b_1}{m} & \frac{m}{3} & 2b_3 & b_4 \\ 0 & 0 & 0 & \frac{3b_0}{m} & 0 & \frac{m}{3} & 2b_3 \\ 0 & 0 & 0 & 0 & 0 & 0 & \frac{m}{3} \end{vmatrix}.$$

Here the denominator N is evidently independent of μ_0 and may be written

$$N = \frac{m}{3}\begin{vmatrix} 1 & 0 & b_4 & 0 \\ \frac{6b_1}{m} & 1 & 2b_3 & b_4 \\ \frac{3b_0}{m} & \frac{6b_1}{m} & \frac{m}{3} & 2b_3 \\ 0 & \frac{3b_0}{m} & 0 & \frac{m}{3} \end{vmatrix} \doteq \frac{m^3}{27} - \frac{(2b_0b_4 + 4b_1b_3)\,m}{3} + $$

$$+ 4b_0b_3^2 + 4b_1^2b_4 + \frac{3b_0^2b_4^2 - 12b_0b_1b_3b_4}{m}.$$

This takes a simpler form if we eliminate all the powers of m except the first. The definition of m gives

$$m^3 = (36b_2^2 - 3b_0b_4 - 12b_1b_3)\,m + 18b_0b_2b_4 - 72b_1b_2b_3$$

$$\frac{1}{m} = \frac{3b_2 - \sqrt{3i_2}}{3\,(4b_1b_3 - b_0b_4)}$$

hence

$$\frac{3b_0^2b_4^2 - 12b_0b_1b_3b_4}{m} = -\,b_0b_4\,(6b_2 - m).$$

With these values, and putting

$$i_3 = b_0b_2b_4 + 2b_1b_2b_3 - b_2^3 - b_0b_3^2 - b_1^2b_4$$

we obtain finally

$$N = \frac{4i_2}{9}\,m - \frac{4}{3}\,(3i_3 + b_2i_2) = \frac{4}{9}\,i_2\sqrt{3i_2} - 4i_3 = \frac{4}{9}\,(i_2\sqrt{3i_2} - 9i_3)\,. \quad (18)$$

Introducing now the values of μ_2 and μ_1 in function of μ_0 in the numerator, we may reduce this to $A\mu_0^2 + B\mu_0 + C$, where the coefficients are to be determined still.

If we put $\mu_0 = 0$, C is immediately found

$$C = -\,a_0 \begin{vmatrix} 1 & 0 & b_4 & 0 \\ \frac{6b_1}{m} & 1 & 2b_3 & b_4 \\ \frac{3b_0}{m} & \frac{6b_1}{m} & \frac{m}{3} & 2b_3 \\ 0 & \frac{3b_0}{m} & 0 & \frac{m}{3} \end{vmatrix} = -\,\frac{3}{m}\,a_0\,N.$$

If we divide further the second and third columns by μ_0 and substitute afterwards $\mu = \infty$, the equation is reducible to

$$A = -\,\frac{m}{3}\,a_0 \begin{vmatrix} \frac{3b_4}{m} & 1 & 0 & 0 \\ \frac{6b_3}{m} & \frac{6b_1}{m} & 1 & b_4 \\ 1 & \frac{3b_0}{m} & \frac{6b_1}{m} & 2b_3 \\ 0 & 0 & \frac{3b_0}{m} & \frac{m}{3} \end{vmatrix} = -\,a_0 \begin{vmatrix} b_4 & 1 & 0 & 0 \\ 2b_3 & \frac{6b_1}{m} & 1 & b_4 \\ \frac{m}{3} & \frac{3b_0}{m} & \frac{6b_1}{m} & 2b_3 \\ 0 & 0 & \frac{3b_0}{m} & \frac{m}{3} \end{vmatrix} = -\,\frac{3}{m}\,a_0 N.$$

Differentiating the numerator with respect to μ_0 and putting $\mu_0 = 0$ afterwards, we find the value of B. This value consists of two determinants; the first of these is identically zero, therefore

$$B = - \left| \begin{array}{ccccccc} a_6 & 1 & 0 & 0 & 0 & 0 & 0 \\ a_5 & \frac{6b_1}{m} & 1 & 0 & 0 & 0 & 0 \\ a_4 & \frac{3b_0}{m} & \frac{6b_1}{m} & 1 & 0 & b_4 & 0 \\ a_3 & 0 & \frac{3b_0}{m} & \frac{6b_1}{m} & 0 & 2b_3 & b_4 \\ a_2 & 0 & 0 & \frac{3b_0}{m} & \frac{3b_4}{m} & \frac{m}{3} & 2b_3 \\ a_1 & 0 & 0 & 0 & \frac{6b_3}{m} & 0 & \frac{m}{3} \\ a_0 & 0 & 0 & 0 & 1 & 0 & 0 \end{array} \right|$$

or

$$\begin{aligned} B = & - a_6 \left[2b_0\, b_1 + \frac{12b_2 - 2m}{4b_1 b_3 - b_0 b_4} (4b_1^3 + b_0^2 b_3 - 6b_0 b_1 b_2) \right] \\ & - a_5 \cdot \frac{2}{3} (b_0 m + 6b_1^2 - 9b_0 b_2) \\ & - a_4 \cdot \frac{2}{3} (b_1 m - 3b_0 b_3) \\ & - a_3 \cdot \frac{2}{3} (b_2 m - 2b_1 b_3 - b_0 b_4) \\ & - a_2 \cdot \frac{2}{3} (b_3 m - 3b_1 b_4) \\ & - a_1 \cdot \frac{2}{3} (b_4 m + 6b_3^2 - 9b_2 b_4) \\ & - a_0 \left[2b_3 b_4 + \frac{12b_2 - 2m}{4b_1 b_3 - b_0 b_4} (4b_3^3 + b_1 b_4^2 - 6b_2 b_3 b_4) \right]. \end{aligned}$$

With these values the differential of Riccati takes the form

$$\mu_0' = - \frac{3}{m} a_6 \mu_0^2 + \frac{B}{N} \mu_0 - \frac{3}{m} a_0 . \quad . \quad . \quad . \quad . \quad (19)$$

and the same reasoning as before shows that if the necessary conditions are satisfied the substitution which reduces the given differential equation (14) to the equation (19) may be inferred from

$$y^3 + \mu_2 y^2 + \mu_1 y + \mu_0 = 0.$$

Substituting the values (17) we conclude finally that

$$\mu_0 = -\frac{my^3 + 6b_1y^2 + 3b_0y}{3b_4y^2 + 6b_3y + m} \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

reduces (14) to (19).

5. To determine in this case the conditions, we differentiate the four values $\frac{b_4}{b_2}$, $\frac{b_3}{b_2}$, $\frac{b_1}{b_2}$, $\frac{b_0}{b_2}$ expressed in λ and μ by (15). This gives

$$\left.\begin{aligned}
6\theta(b_4b_2') &= (6b_2\mu_2 - 3b_4\mu_0)\lambda_3' - (b_4\mu_1 + 6b_2)\lambda_2' + b_4\mu_2\lambda_1' + 3b_4\lambda_0' + \\
&\quad + (b_4\lambda_1 + 6b_2\lambda_3)\mu_2' - b_4\lambda_2\mu_1' - 3b_4\lambda_3\mu_0' \\
6\theta(b_3b_2') &= (3b_2\mu_1 - 3b_3\mu_0)\lambda_3' - b_3\mu_1\lambda_2' + (b_3\mu_2 - 3b_2)\lambda_1' + 3b_3\lambda_0' + \\
&\quad + b_3\lambda_1\mu_2' + (3b_2\lambda_3 - b_3\lambda_2)\mu_1' - 3b_3\lambda_3\mu_0' \\
6\theta(b_1b_2') &= -3b_1\mu_0\lambda_3' + (3b_2\mu_0 - b_1\mu_1)\lambda_2' + b_1\mu_2\lambda_1' + (3b_1 - 3b_2\mu_2)\lambda_0' + \\
&\quad + (b_1\lambda_1 - 3b_2\lambda_0)\mu_2' - b_1\lambda_2\mu_1' + (3b_2\lambda_2 - 3b_1\lambda_3)\mu_0' \\
6\theta(b_0b_2') &= -3b_0\mu_0\lambda_3' - b_0\mu_1\lambda_2' + (b_0\mu_2 + 6b_2\mu_0)\lambda_1' + (3b_0 - 6b_2\mu_1)\lambda_0' + \\
&\quad + b_0\lambda_1\mu_2' - (b_0\lambda_2 + 6b_2\lambda_0)\mu_1' + (6b_2\lambda_1 - 3b_0\lambda_3)\mu_0'
\end{aligned}\right\} \quad . \quad (21)$$

Combining each of these equations with the seven former equations (15) and eliminating the quantities $\lambda_3'\,\lambda_2'\,\lambda_1'\,\lambda_0'\,\mu_2'\,\mu_1'\,\mu_0'$, we obtain

$$\begin{vmatrix}
a_6 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
a_5 & \mu_2 & 1 & 0 & 0 & -\lambda_3 & 0 & 0 \\
a_4 & \mu_1 & \mu_2 & 1 & 0 & -\lambda_2 & -\lambda_3 & 0 \\
a_3 & \mu_0 & \mu_1 & \mu_2 & 1 & -\lambda_1 & -\lambda_2 & -\lambda_3 \\
a_2 & 0 & \mu_0 & \mu_1 & \mu_2 & -\lambda_0 & -\lambda_1 & -\lambda_2 \\
a_1 & 0 & 0 & \mu_0 & \mu_1 & 0 & -\lambda_0 & -\lambda_1 \\
a_0 & 0 & 0 & 0 & \mu_0 & 0 & 0 & -\lambda_0 \\
C_0 & C_1 & C_2 & C_3 & C_4 & C_5 & C_6 & C_7
\end{vmatrix} = 0$$

where the last row is formed by the coefficients of each of the four equations (21). Hence for the first of these

$$C_0 = 6(b_4b_2'), \qquad C_1 = 6b_2\mu_2 - 3b_4\mu_0, \text{ etc.}$$

If we reduce this determinant in the same way as before, the last row becomes in the first place

$$C_0,\ C_1,\ C_2,\ C_3,\ C_4,\ \frac{\lambda_3C_2 + C_5}{\theta},\ \frac{\lambda_3C_3 + C_6}{\theta},\ \frac{\lambda_3C_4 + C_7}{\theta}$$

and secondly

$$C_0,\ C_1,\ C_2-\frac{3\mu_0}{m}\frac{\lambda_2 C_2+C_5}{\theta},\ C_3-\frac{3\mu_0}{m}\frac{\lambda_2 C_3+C_6}{\theta},\ C_4-\frac{3\mu_0}{m}\frac{\lambda_2 C_4+C_7}{\theta},$$
$$\frac{\lambda_2 C_2+C_5}{\theta},\ \frac{\lambda_2 C_3+C_6}{\theta},\ \frac{\lambda_2 C_4+C_7}{\theta},$$

that is for the four cases successively

$$6\,(b_4 b_2'),\ 6\,b_2\mu_2-3b_4\mu_0,\ -6\,b_2-\frac{3b_0 b_4}{m},\ \frac{6b_1 b_4}{m},\ 3b_4,\ -2b_3 b_4,\ b_4^2,\ 0$$

$$6\,(b_3 b_2'),\ 3\,b_2\mu_1-3b_3\mu_0,\ -\frac{3b_0 b_3}{m},\ \frac{6b_1 b_3}{m}-3b_2,\ 3b_3,\ -2b_3^2,\ b_3\,b_4,\ 0$$

$$6\,(b_1 b_2'),\ -3\,b_1\mu_0,\ -\frac{3b_0 b_1}{m},\ \frac{6b_1^2}{m},\ 3b_1-\frac{18b_1 b_2}{m},\ b_2 m-2b_1 b_3,\ b_1 b_4,\ -3b_2 b_4$$

$$6\,(b_0 b_2'),\ -3\,b_0\mu_0,\ -\frac{3b_0^2}{m},\ \frac{6b_0 b_1}{m},\ 3b_0-\frac{18b_0 b_2}{m},$$
$$-2b_0 b_3,\ b_0 b_4+2b_2 m,\ -12b_2 b_3$$

which may be represented for a moment by $D_0\,D_1\,D_2\,D_3\,D_4\,D_5\,D_6\,D_7$. After these reductions it is evident that only the second column contains the quantities $\mu_0\,\mu_1\,\mu_2$. Hence, with regard to the relations (17), this determinant may be written in the form $A\mu_0+B$, where the value of A is found by differentiating with respect to μ_0 and B by substituting $\mu_0=0$.

In this way A takes the form of a determinant of the eighth order which immediately leads to the following of the sixth order.

$$A=-a_3 u\begin{vmatrix} \frac{3b_4}{m} & 1 & 0 & 0 & 0 & 0 \\ \frac{6b_3}{m} & \frac{6b_1}{m} & 1 & 0 & b_4 & 0 \\ 1 & \frac{3b_0}{m} & \frac{6b_1}{m} & 1 & 2b_3 & b_4 \\ 0 & 0 & \frac{3b_0}{m} & \frac{6b_1}{m} & \frac{m}{3} & 2b_3 \\ 0 & 0 & 0 & \frac{3b_0}{m} & 0 & \frac{m}{3} \\ D_1' & D_2 & D_3 & D_4 & D_5 & D_6 \end{vmatrix}=a_3 u\left(\frac{3}{m}\right)^4\begin{vmatrix} \frac{m}{3}D'_1 & \frac{m}{3}D_2 & \frac{m}{3}D_3 & \frac{m}{3}D_4 & D_5 & D_6 \\ b_4 & \frac{m}{3} & 0 & 0 & 0 & 0 \\ 2b_3 & 2b_1 & \frac{m}{3} & 0 & b_4 & 0 \\ \frac{m}{3} & b_0 & 2b_1 & \frac{m}{3} & 2b_3 & b_4 \\ 0 & 0 & b_0 & 2b_1 & \frac{m}{3} & 2b_3 \\ 0 & 0 & 0 & b_0 & 0 & \frac{m}{3} \end{vmatrix}$$

where $D_1'=\dfrac{dD_1}{d\mu_0}$.

Developing this determinant, and putting

$$\frac{m^4}{81}-\frac{4b_1b_3+2b_0b_4}{9}m^2+\frac{4b_0b_3^2+4b_1^2b_4}{3}m+b_0b_4(b_0b_4-4b_1b_3)=P$$

we have

$$A=a_6u\left(\frac{3}{m}\right)^4P\left[\frac{m^2}{9}D_1'-\frac{b_4m}{3}D_2-\frac{2b_3m}{3}D_3-\frac{m^2}{9}D_4+2b_1D_5+b_0D_6\right].$$

If we introduce now the values of the quantities D in the last factor, this leads in the four different cases to

$$-\frac{2b_4}{3}m^3+4b_2b_4m+2b_4(b_0b_4-4b_1b_3)$$

$$-\frac{2b_3}{3}m^3+4b_2b_3m+2b_3(b_0b_4-4b_1b_3)$$

$$-\frac{2b_1}{3}m^3+4b_1b_2m+2b_1(b_0b_4-4b_1b_3)$$

$$-\frac{2b_0}{3}m^3+4b_0b_2m+2b_0(b_0b_4-4b_1b_3).$$

If we observe that we have by definition

$$b_0b_4-4b_1b_3=\frac{m^2-6b_2m}{3}$$

it is evident that in all cases $A=0$.

The conditions are therefore determined by $B=0$, and this may be written, after a slight reduction

$$\begin{vmatrix}
a_6 & \frac{m}{3} & 0 & 0 & 0 & 0 & 0 & 0 \\
a_5 & 2b_1 & \frac{m}{3} & 0 & 0 & 0 & 0 & 0 \\
a_4 & b_0 & 2b_1 & \frac{m}{3} & 0 & b_4 & 0 & 0 \\
a_3 & 0 & b_0 & 2b_1 & \frac{m}{3} & 2b_3 & b_4 & 0 \\
a_2 & 0 & 0 & b_0 & 2b_1 & \frac{m}{3} & 2b_3 & b_4 \\
a_1 & 0 & 0 & 0 & b_0 & 0 & \frac{m}{3} & 2b_3 \\
a_0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{m}{3} \\
D_0 & \frac{m}{3}(D_1)_0 & \frac{m}{3}D_2 & \frac{m}{3}D_3 & \frac{m}{3}D_4 & D_5 & D_6 & D_7
\end{vmatrix}=0$$

where the elements of the last row are respectively in the four cases :

$6(b_4b_2'),\ 12b_1b_2,\ -(b_0b_4+2b_2m),\ 2b_1b_4,\ b_4m,\ -2b_3b_4,\ b_4^2,\ 0$

$6(b_3b_2'),\ 3b_0b_2,\ -b_0b_3,\ 2b_1b_3-b_2m,\ b_3m,\ -2b_3^2,\ b_3b_4,\ 0$

$6(b_1b_2'),\ 0,\ -b_0b_1,\ 2b_1^2,\ b_1(m-6b_2),\ b_2m-2b_1b_3,\ b_1b_4,\ -3b_2b_4$

$6(b_0b_2'),\ 0,\ -b_0^2,\ 2b_0b_1,\ b_0(m-6b_2),\ -2b_0b_3,\ b_0b_4+2b_2m,\ -12b_2b_3$

6. Following the same way in the general case, we obtain for μ_0' the quotient of two determinants each of order $2n+1$. If we reduce these as before, the denominator will be seen to be independent of λ and μ; and the numerator will only contain the quantities $\mu_{n-1}, \mu_{n-2} \cdot\cdot \mu_1, \mu_0$ in two columns. Now $\mu_{n-1}, \mu_{n-2}, \cdot\cdot \mu_1$ may be expressed as linear functions of μ_0, and this proves at once that the numerator must be a polynomial of the second degree in μ_0. If, therefore the necessary conditions are satisfied, the quantity μ_0 is an integral of an equation of RICCATI. The substitution which reduces the given differential equation to this equation of RICCATI will then be found from

$$y^n + \mu_{n-1}\, y^{n-1} + \dots \mu_1\, y + \mu_0 = 0$$

by determining $\mu_{n-1}, \dots \mu_1$ in function of μ_0 and expressing μ_0 in function of y.

Physics. — *"The law of shift of the central component of a triplet in a magnetic field."* By Prof. P. ZEEMAN.

In two communications to this Academy [1]) on "Change of wavelength of the middle line of triplets" I gave conclusive evidence obtained by means of MICHELSON's echelon-spectroscope that the central line of some triplets is shifted. The fact of this displacement was established simultaneously with my own observations by GMELIN [2]) and JACK [3]). GMELIN first gave the law of shift in the case of the mercury line 5791. According to him the change of wavelength under consideration is proportional to the square of the magnetic force.

In the second part of a former paper on "Magnetic resolution of spectral lines and magnetic force" measurements concerning the asymmetrical resolution of the mercury line 5791 are given [4]).

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[1]) P. ZEEMAN. These Procedings February 1908, April 1908.

[2]) GMELIN. Physikalische Zeitschrift. 9. Jahrgang S. 212—214. 1908.

[3]) JACK see VOIGT. Magneto-optik. S. 178.

[4]) ZEEMAN. These Proceedings November 1907.

Supposing that the asymmetry of the separation is entirely due to the shift of the central line towards the red, one should conclude from the communicated numbers that the displacement increases nearly linearly with the strength of field. This investigation was made with ROWLAND's grating, the principal object in view being to prove the existence of asymmetrical separations. I succeeded in this respect, but I think now I have overrated the accuracy of the extremely difficult determinations of the amount of the asymmetry. In fields of the order of 20000 gauss the asymmetry is 35 thousandth parts of an Ångström unit, while the ROWLAND grating used permits in the chosen, first order to resolve lines, the difference of whose wavelengths is 0.12 Å.U., hence with the field intensities mentioned we have to do with a quantity which is already four times smaller than the limit imposed by the resolving power.

It is only because we have to do in determining the asymmetry with a difference of two quantities which are above the limit set by the resolving power, that there may be question of measurement.

When we reach however the utmost limits of the method used then sources of error come to the front, which partly are caused by our mode of appreciation of the distance of two adjacent lines, partly are connected with particularities in the formation of images by gratings, not yet sufficiently understood.

It is therefore undoubtedly to be preferred to use for the further investigation of the shift of the central line a method warranting greater resolving power. GMELIN in his investigation has used MICHELSON's echelon grating, and it seems that he has largely succeeded by systematic procedure to interprete quantitatively the results given by this instrument. His result therefore possesses high probability and moreover is now supported by the theory given by VOIGT [1]) in order to explain the large asymmetrical separations, a theory which assumes the existence of couplings between the electrons.

I thought it however to be worth while to investigate the matter by a method independent of ROWLAND's and MICHELSON's apparatus. FABRY and PEROT's method seemed most appropriate. The greater part of the measurements communicated in this paper have been obtained with a 5 m.m. étalon, already used on a former occasion. Some determinations were made with an étalon with distance-pieces of *invar* as suggested by FABRY and PEROT in order to diminish the dependence upon temperature. It was constructed for me by JOBIN.

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[1]) VOIGT. Magneto-optik. S. 261.

The thickness of the air-layer in this étalon was nearly 25 m.m. With this distance and using the light of the mercury line 5790 in the magnetic field the limit of the method is being rapidly approached. Hence the accuracy of the results obtained with the 25 m.m. étalon is in our case hardly superior to that to be reached with the 5 m.m. apparatus.

The arrangement of the apparatus was described with sufficient detail on a former occasion[1]). For the purpose now in view it was desirable to investigate exclusively the vibrations parallel to the magnetic force. A calcspar-rhomb therefore was placed between the source of light and the first lens. Two images of the radiating vacuum-tube are now obtained near together on the étalon, the non-desired one being screened off. A photograph was taken with the field on, and before and afterwards one with the field off.

Besides the inner ring, always also the second- ring, in some cases also the third and fourth one, was measured and the result used in the wave-length calculation.

The formula for the calculation is the one first given by FABRY and PEROT, still remarkably simplified in our case [2]).

In the following table the results are given relating to the mercury line 5791. The first column contains the number of the experiment, the second one the reference-number of the spectrogram; $\Delta\lambda_0$ is the change of wavelength of the central component. The field intensities are given in the last column. Their *relative* values, which are only necessary for establishing the law connecting displacement and strength of field, are exact. These numbers must be increased with 1 or 2°/₀ in order to reduce them to gausses.

Experiment	Plate n°.	$\Delta\lambda_0$ in A. U.	H.
1	208^c	0.0085	12700
2	209^b	0.0088	12700
3	211	0.0169	20700
4	212^c	0.0074	13950
5	214^c	0.0201	20600
6	218^b	0.0367	28250
7	218^d	0.0358	28250
8	219^b	0.0360	28250
9	220^b	0.0353	29170
10	220^d	0.0406	29780

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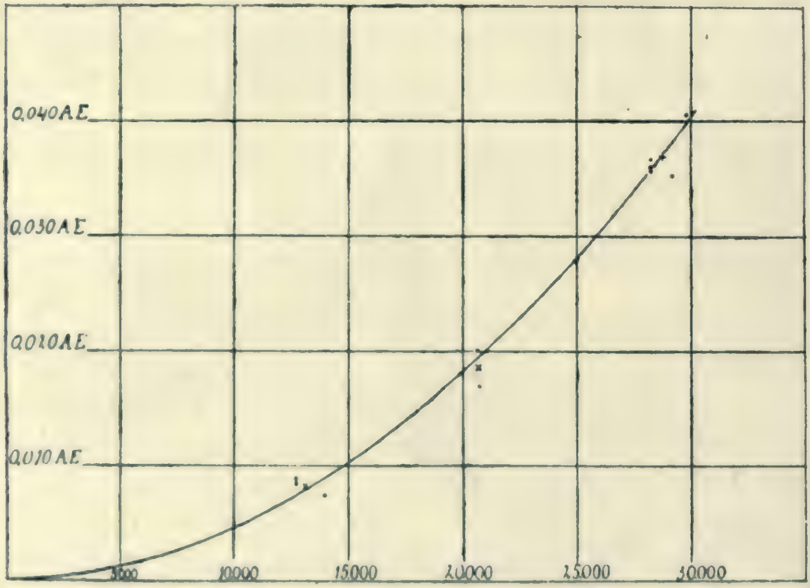
[1]) ZEEMAN. These Procee dings December 1907.

[2]) See These Proceedings December 1907, February 1908.

The experiments 4 and 5 are made with the 25 m.m. étalon, the other ones with the 5 mm. apparatus. In the figure the results are graphed. The smallness of the displacements may be illustrated by the statement, that the outer components of the triplet 5791 are separated 0.500 A.U. from the unmodified position in a field of 29750 Gauss. The ordinate measuring 0.500 A.U. would be 75 cm. in the figure.

The results 1, 2 and 4; 3 and 5; 6, 7, 8, 9, 10 were combined in each case by assigning simply to each mean displacement the mean magnetic intensity. The three principal values, thus obtained are indicated by crosses. These points and the origin lie very approximately on a parabola.



Inspection of the figure or a simple calculation easily shows that the quadratic law is obeyed within the limits of the errors of observation of the measured displacements. The magnitude of the displacement has been measured in the average in each of the ten points to within 0.002 or 0.003 Å.U.

In order to show how the values of $\Delta\lambda_0$ were obtained, I will give the calculation of one case in full.

$$\lambda_m - \lambda_0 = \frac{\lambda_0}{8R^2}(x_0^2 - x_m^2)$$

$$\lambda_0 = 5791 \text{ Å. E. } H = 12700$$

$$\text{Etalon } 2\,d = 10\,m.m. \quad R = 120\,m.m.$$

x_0 , x_m diameters of the rings in $m.m.$

x_0 mean of 2 diameters on plates taken before and after x_m.

$$\left.\begin{array}{lll} \text{First ring:} & & \\ x_0 = 3.662 & x_0^2 = 13.410 & \\ & & 0.160 \\ x_m = 3.640 & x_m^2 = 13.250 & \\ \text{Second ring:} & & \\ x_0 = 2.608 & x_0^2 = 6.802 & \\ & & 0.182 \\ x_m = 2.573 & x_m^2 = 6.620 & \end{array}\right\} 0.171$$

$$\Delta \lambda_0 = \frac{0.171 \lambda_0}{8 R^2} = 0.0086 \text{ Å. E.}$$

In the case of the triplet of the mercury line 5770 no displacement of the central line could be found. In a field of 28250 the following values of the diameters were obtained with the 5 m.m. étalon:

First ring	Second ring	
2.199	3.409	field off.
2.193	3.408	field on.
2.199	3.394	field off.

Hence the central line of 5770 remains within the limits of experimental error exactly in the position of the unmodified one.

Physics. — "*Contribution to the theory of binary mixtures,*" XII. (Continued). By Prof. J. D. VAN DER WAALS.

In the discussion in the preceding contribution on the question whether there is any possibility that values of $v > b_2$ might occur in the case that the locus of the points of intersection of the curves $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ is a closed curve, we have also discussed (p. 433) the case that (φ''') or:

$$n - 1 - n \sqrt{\left\{A - x\frac{dA}{dx}\right\}} \mp \sqrt{\left\{A + (1-x)\frac{dA}{dx}\right\}} = 0$$

would be imaginary over the full width from $x = 0$ to $x = 1$. We have reduced this equation there to the following form:

$$n - 1 - nx \sqrt{\frac{c}{a}\,\frac{a_2 - c(1-x)^2}{a}} \mp (1-x) \sqrt{\frac{c}{a}\,\frac{a_1 - cx^2}{a}} = 0$$

and shown that if $n > 2$, the value of $a_1 - cx^2$ may become negative for the high values of x. The limiting value of x is then equal to $\sqrt{\frac{a_1}{c}}$, so that we have $x_g = \sqrt{\frac{a_1}{c}}$. We then observed (p. 435) that if such a limiting value for x exists, our conclusion that $\varphi''' = 0$ must possess a minimum value which is negative, can no longer be considered as proved; but we omitted the observation that the thesis that v would have to be $< b_2$, may not be considered as proved any longer either. If viz. the substitution of $x = x_g$ should make the first member of (φ''') negative, whereas, as we saw before, the substitution of $x = 0$ makes the first member of (φ''') positive, then a value of x must exist which makes (φ''') $= 0$ both on the branch of (φ''') with the negative sign for the third term as on that with the positive sign. Then it is therefore unnecessary, that (φ''') possesses a minimum value, and there is no reason for the positive sign for the third term, and so no necessity for v being smaller than b_2.

Let us seek the condition for:

$$n - 1 - nx_g \frac{\sqrt{\{a_2 - c\,(1-x_g)^2\}}}{a} < 0$$

or

$$\frac{n-1}{n} < \frac{x_g \sqrt{\frac{a_2}{c} - (1-x_g)^2}}{\frac{a}{c}}$$

Let us write;

$$\frac{a}{c} = \frac{a_1}{c}(1-x_g) + \frac{a_2 x_g}{c} - x_g(1-x_g)$$

or

$$\frac{a}{c} = x^2{}_g(1-x_g) + \frac{a_2 x_g}{c} - x_g(1-x_g)$$

or

$$\frac{a}{c} = x_g \left\{\frac{a_2}{c} - (1-x_g)^2\right\}.$$

The condition put above, becomes then:

$$\frac{n-1}{n} < \frac{1}{\sqrt{\left\{\frac{a_2}{c} - (1-x_g)^2\right\}}}$$

or

$$\frac{a_2}{c} - (1-x_g)^2 < \frac{n^2}{(n-1)^2}$$

or

$$\frac{n^2(1+\varepsilon_2)}{(n-1)^2} - (1-x_g)^2 < \frac{n^2}{(n-1)^2}$$

or

$$\frac{n^2\varepsilon_2}{(n-1)^2} - (1-x_g)^2 < 0$$

or

$$\frac{n\sqrt{\varepsilon_2}}{n-1} < 1-x_g.$$

And taking into account that $x_g = \sqrt{\frac{a_1}{c}} = \frac{\sqrt{1+\varepsilon_1}}{n-1}$, we obtain as condition:

$$(n-1) > \sqrt{1+\varepsilon_1} + n\sqrt{\varepsilon_2}.$$

I have given it in this form in the "Erratum" accompanying the preceding Contribution.

Before discussing the signification of this condition I will remark that we might, indeed, have obtained this result in a less intricate way.

Let us directly put the value $v = b_2$ in the equation for the closed curve, and let us examine what value of x then satisfies the equation. If $v = b_2$, then $v-b = (b_2-b_1)(1-x)$, and $v^2 = b_2^2$. Equation (α) of Contribution X p. 318 becomes then:

$$\frac{(n-1)^2}{n^2}(1-x) = \frac{c\,x\,(1-x)}{a}$$

or

$$\frac{(n-1)^2}{n^2 x} = \frac{c}{a} = \frac{1}{\frac{a_1}{c}(1-x) + \frac{a_2}{c}x - x(1-x)}$$

or

$$\frac{1}{n^2 x} = \frac{1}{(1+\varepsilon_1)(1-x) + n^2(1+\varepsilon_2)x - x(1-x)(n-1)^2}$$

then we find as condition for the calculation of x for which $v = b_2$:

$$\frac{1+\varepsilon_1}{(n-1)^2}(1-x) + \frac{n^2\varepsilon_2}{(n-1)^2}x - x(1-x) = 0$$

or

$$x^2 - x\left\{1 + \frac{1+\varepsilon_1-n^2\varepsilon_2}{(n-1)^2}\right\} + \frac{1+\varepsilon_1}{(n-1)^2} = 0 \quad . \quad . \quad . \quad . \quad (\beta)$$

As $1+\varepsilon_1$ must certainly be positive, because a negative value of a_1 is inconceivable, we see that if the above equation has real roots, it must have two for positive values of x in all possible cases, also if ε_1 and ε_2 should be negative. The condition for the roots being real is:

$$1+\frac{1+\varepsilon_1-n^2\varepsilon_2}{(n-1)^2}>\frac{2\sqrt{1+\varepsilon_1}}{n-1}$$

or

$$1-\frac{\sqrt{(1+\varepsilon_1)}}{n-1}>\frac{n\sqrt{\varepsilon_2}}{n-1}.$$

So the same condition as had been found above.

If we represent the condition for the possibility of $v > b_2$ again graphically, it is given by a parabola, and that the same as occurs in fig. 36 p. 321, but shifted downward in the direction of the ε_1-axis by an amount $=1$. We need not draw it, but we shall think the points of contact with the ε_1-axis and with a line $\varepsilon_1 = -1$ indicated by the letters Q'' and P''. To satisfy the circumstance $v > b_2$, the point $(\varepsilon_1, \varepsilon_2)$ must lie inside the space which I shall call $O''P''Q''$. But for the possibility of the closed figure the point $(\varepsilon_1, \varepsilon_2)$ must lie inside the space OPQ — in both cases below the corresponding parabola. This can only occur when the two areas mentioned cover each other or as least overlap. This requires $(n-1)^2 > 1$ or $n > 2$. So the points $(\varepsilon_1, \varepsilon_2)$ giving a closed curve, for which the value $v > b_2$ occurs between two values of x, are confined to a smaller space, again bounded by the axes and a parabola. In this case the parabola touches the ε_1-axis at a distance $n(n-2)$ from the origin, but intersects the ε_2-axis at a distance $=\frac{n(n-2)}{n^2}=\frac{n-2}{n}$ from the origin. The condition that the two values of x for which $v = b_2$, coincide, and that the closed curve touch a line $v = b_2$ is this: that the point $(\varepsilon_1, \varepsilon_2)$ shall lie on this parabola. Then $x=\sqrt{\frac{1+\varepsilon_1}{(n-1)^2}}$ and $1-x=\frac{n\sqrt{\varepsilon_2}}{n-1}$. If we compare this value of x with that which we have called x_g above, x_g appears to be besides highest value of x for which $\frac{dv}{dx}$ is equal to 0 for the points of the closed curve, also the value of x for the point in which the closed curve touches the line $v = b_2$. If volumes occur which are larger than b_2, then the greatest volume lies at a value of $x < x_g$.

Let us now more closely examine the space which OPQ and $O''P''Q''$ have in common, and inside which the points $(\varepsilon_1, \varepsilon_2)$ must lie for the condition $v > b_2$ to be satisfied. For n very large this space will be very large in the direction of the ε_1-axis, but in the direction of the ε_2-axis it remains limited to an amount $1-\frac{2}{n}$ and so below unity. Also by simple construction we can now indicate a rule for the place of the points (ε_1, ε_2) which satisfy the requirement that the portion cut off by the closed curve from the line $v = b_2$, have a given value.

From equation (β) of p. 479 follows:

$$2x = 1 + \frac{1+\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2} \pm \sqrt{\left\{\left[1 + \frac{1+\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2}\right]^2 - 4\,\frac{1+\varepsilon_1}{(n-1)^2}\right\}}$$

If we represent the highest value of x by x_2, and the smallest by x_1, then:

$$(x_2 - x_1)^2 = \left[1 + \frac{1+\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2}\right]^2 - 4\,\frac{1+\varepsilon_1}{(n-1)^2}$$

or

$$2\sqrt{\left\{\frac{1+\varepsilon_1}{(n-1)^2} + \frac{(x_2-x_1)^2}{4}\right\}} = 1 + \frac{1+\varepsilon_1}{(n-1)^2} + \frac{(x_2-x_1)^2}{4} - n^2\left\{\frac{\varepsilon_2}{(n-1)^2} + \frac{(x_2-x_1)^2}{4n^2}\right\}$$

or

$$1 - \sqrt{\left[\frac{1+\varepsilon_1}{(n-1)^2} + \frac{(x_2-x_1)^2}{4}\right]} = n\sqrt{\left[\frac{\varepsilon_2}{(n-1)^2} + \frac{(x_2-x_1)^2}{4n^2}\right]}$$

So the points for which $x_2 - x_1$ has an equal value, lie again on a parabola, and one of the same shape as that of fig. 36; but now it has undergone two shiftings.

The first shifting is that in which all the points of the parabola have descended by an amount $= 1$ in the direction of the ε_1-axis which makes it the upper limit of the space now under discussion. But the second shifting is one which takes place in the direction of the diameter or the axis of the parabola. The amount of the second shifting must be such that it can be considered as the resultant of a displacement in the direction of the negative ε_1 by an amount equal to $\frac{(x_2-x_1)^2}{4}(n-1)^2$ and a displacement in the direction of the negative ε_2-axis by an amount equal to $\frac{(x_2-x_1)^2}{4}\frac{(n-1)^2}{n^2}$. According as $x_2 - x_1$ is greater, this second shifting is more considerable — but as soon as the shifting would proceed so far that the parabola would have no more points inside the original space OPQ we have exceeded the possible value of $x_2 - x_1$. The extreme limits of $x_2 - x_1$ are then on one side 0, and on the other side $1 - \frac{1}{n-1} = \frac{n-2}{n-1}$. This greatest value of $x_2 - x_1$, which is equal to 0 for $n = 2$ itself approaches 1 with increasing value of n. We may also express the above as follows. When we have a point $(\varepsilon_1, \varepsilon_2)$ in the space which OPQ and $O''P''Q''$ have in common, the closed curve will possess volumes which are greater than b_2 — and by shifting this point in the direction of the axis of the parabola till it meets the first-mentioned shifted parabola, we find the value $\frac{(x_2-x_1)^2}{4}(n-1)^2$, in the projection of this displacement on the ε_1-axis, or the value of $\frac{(x_2-x_1)^2}{4}\frac{(n-1)^2}{n^2}$ in the projection of this displacement on the ε_2-axis. So the length of the line drawn through the given point in the direction of the axis of the parabola till it meets the second parabola teaches us the value of $(x_2-x_1)^2$; to which we may add that the same line prolonged to the other side so below the given point, shows us also at what value of x the middle of x_1 and x_2 lies. If the continuation of this line passes through the point $\varepsilon_2 = 0$ and $\varepsilon_1 = -1$, the middle of x_1 and x_2 lies exactly at $x = \frac{1}{2}$. If this line intersects the ε_1-axis below $\varepsilon_1 = -1$, then $\frac{x_1+x_2}{2} < \frac{1}{2}$ and the other way about. We have viz. from (β):

$$x_1 + x_2 = 1 + \frac{1+\varepsilon_1 - x^2\varepsilon_2}{(n-1)^2},$$

or putting $\frac{x_1+x_2}{2} = x_m$:

$$1 - 2x_m = -\frac{1+\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2}.$$

For given value of x_m this represents a straight line, the direction of which is given by $\frac{\varepsilon_1}{\varepsilon_2} = n^2$. This straight line intersects the ε_1-axis in a point $\varepsilon_1 + 1 = -(n-1)^2(1-2x_m)$; from this formula the given rule appears.

Such rules may also be given for the dimension and the place of the closed curve itself — and for the accurate knowledge of the properties of this curve the knowledge of such rules is not devoid of importance. Thus the equation (β') of p. 319 Contribution X leads to:

$$(x_2-x_1)^2 = \left\{1 + \frac{\varepsilon_1 - n^2\varepsilon_2}{(n-1)^2}\right\}^2 - \frac{4\varepsilon_1}{(n-1)^2}$$

when the values of x between which the curve exists, are represented by x_1 and x_2. If we derive from this:

$$1-\sqrt{\left\{\frac{\varepsilon_1}{(n-1)^2}+\frac{(x_2-x_1)^2}{4}\right\}}=n\sqrt{\left\{\frac{\varepsilon_2}{(n-1)^2}+\frac{(x_2-x_1)^2}{4n^2}\right\}}$$

it appears that the locus of the points ε_1 and ε_2 for which the closed curve has the same width, is again the same parabola *OPQ*, but shifted in opposite direction of the axis by an amount of such a value that the projection on the ε_1-axis is equal to $(n-1)^2 \frac{(x_2-x_1)^2}{4}$. For the points of *OPQ* itself the width is, therefore, equal to 0, and for the origin, in which ε_1 and ε_2 is equal to 0, $x_2-x_1=1$, and the curve occupies the whole width. The decrease of the values of ε_1 and ε_2 obtained by shifting in the opposite direction of the axis of the parabola, promotes therefore the intersection of $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}=0$, and so furthers the non-miscibility. In the same way we find, representing the value of $\frac{x_1+x_2}{2}$ by x_m:

$$1-2x_m=-\frac{\varepsilon_1-n^2\varepsilon_2}{(n-1)^2}.$$

So if we trace a line parallel to the axis of the parabola through the origin, this line is the boundary for the points for which $x_m \gtrless \frac{1}{2}$

For the points for which $\varepsilon_1 > n^2\varepsilon_2$, $x_m > \frac{1}{2}$, and the other way about.

And finally this property. We may also write the equation (β') of p. 319 Contribution X indicating the limiting value of x which corresponds to given value of ε_1 and ε_2 as follows:

$$\frac{\varepsilon_1}{(n-1)^2}\frac{1}{x}+\frac{n^2\varepsilon_2}{(n-1)^2}\frac{1}{1-x}=1.$$

Let $x=x_1$ for one of these limiting values, then this equation becomes:

$$\frac{\varepsilon_1}{(n-1)^2}\frac{1}{x_1}+\frac{n^2\varepsilon_2}{(n-1)^2}\frac{1}{1-x_1}=1$$

And for constant value of x_1, this last formula represents a straight line for the points $(\varepsilon_1, \varepsilon_2)$. On this straight line also the point must lie for which not only the one limiting value of $x=x_1$, but also the second, and for which the two values of x therefore coincide. In this case $x_1=\frac{\sqrt{\varepsilon_1}}{n-1}$ and $1-x_1=\frac{n\sqrt{\varepsilon_2}}{n-1}$. Hence we get back again the limiting relation between ε_1 and ε_2 or in other words the equation of the parabola by this substitution in the equation of the straight line. So this straight line is a tangent to the parabola, and one touching in the point in which also the second limiting value of x, or x_2 coincides with x_1. From this follows then this rule. If we draw a tangent to the parabola in the area OPQ, then all the points $(\varepsilon_1, \varepsilon_2)$ for which one of the limiting values is equal to the value for x of the point of contact, lie on this tangent. If we draw a second tangent to the parabola, the point of intersection with the first tangent has the property that the values of x of the two points of contact belong to it for x_1 and x_2. If we have drawn one tangent, tangents may be drawn from all the points of this line lying on the lefthand side of the point of contact, so from all the points for which ε_2 is smaller, and ε_1 larger than that of the point of contact, to the points for which ε_1 is larger, and so $x_2 > x_1$, and the other way about. If we wish to indicate in what part of the space OPQ below the parabola the points lie for which the values of ε_1 and ε_2 are such that the whole closed curve remains restricted either to values of $x > \frac{1}{2}$ or to values of $x < \frac{1}{2}$, we must begin with finding the point on the parabola for which $x_1 = x_2 = \frac{1}{2}$. This is the point for which $\varepsilon_1 = n^2\varepsilon_2$, and which therefore lies on the line which is drawn from the origin in the direction of the axis of the parabola. In this point we must trace the tangent to the parabola. From the ε_1-axis this tangent cuts off a portion $= \frac{(n-1)^2}{2}$ and from the ε_2-axis a portion $= \frac{(n-1)^2}{2n^2}$. So it is a line parallel to the straight line PQ of fig. 36, and it cuts off from the axes parts equal to $\frac{OP}{2}$ and $\frac{OQ}{2}$. This tangent divides the space OPQ below the parabola into three parts, viz. the part below this tangent, and the two other parts above this tangent and further bounded by the parabola and one of the axes. The righthand one of these two parts contains the points, for which the closed curve remains confined to values of $x < \frac{1}{2}$. For the lefthand part the reverse applies..

So according to this result either of these cases would be possible either that the closed curve remains restricted to values of $x > \frac{1}{2}$, or to values of $x < \frac{1}{2}$. But if it is asked whether it is probable that both cases occur, this probability depends on the value which l^2 must assume in these two cases. The point in which these spaces touch, is the point where $\varepsilon_1 = n^2 \varepsilon_2 = \frac{(n-1)^2}{4}$. For this point to be possible the following equation must hold:

$$(2n + \varepsilon_1 + n^2 \varepsilon_2)^2 = 4 l^2 (1 + \varepsilon_1) n^2 (1 + \varepsilon_2)$$

We find from this by substitution of the values ε_1 and ε_2:

$$l^2 = \frac{(n+1)^4}{(n+1)^4 + 4(n-1)^4}.$$

So in any case a value of $l^2 < 1$. It becomes smaller as n increases, and the limiting value for $n = \infty$ amounts to $\frac{1}{5}$. Such a small value, however, l^2 will most likely never assume. And if we now take into consideration that for the points of the lefthand part, for the points of which $x > \frac{1}{2}$, the value of l^2 will have to be still smaller, we arrive at the conclusion that if n is large, the case that the closed curve remains restricted to values of $x > \frac{1}{2}$ will not have much chance of occurring. For the point in which the two spaces touch l^2 is equal to $\frac{81}{85}$ for $n = 2$, and this value is equal to $\frac{4}{5}$ for $n = 3$, and we may consider these values of l^2 as probably possible. So that we arrive at the conclusion that for not great values of n, e.g. $n = 3$, the closed curve, if it exists, can occur at $x > \frac{1}{2}$, but that for higher values of n, and also if l^2 should be > 1, the other case, $x < \frac{1}{2}$, is possible.

Let us now proceed to derive some results on the miscibility or non-miscibility in the liquid state from what has been observed on the intersection of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$, for the case that the locus of the points of intersection is a closed curve, and to compare these results with the observed facts. All the properties discussed of the closed curve are perhaps no longer necessary if we could have anticipated this result. They have, however, been necessary for me to come to this conclusion. And if we do not content ourselves with more or less vague indications, but want to give clearly defined statements, the knowledge of most of the properties discussed is necessary.

I already treated one of the meanings of the closed curve, p. 331 Contribution X. In this case contact of $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}=0$ occurs for the first time at low temperature T_2; at rising temperature there is intersection of these two curves. But with further rise of T the two points of intersection draw nearer together, and at $T=T_1$ there is again contact. For the case mentioned $\frac{d^2\psi}{dx^2}=0$ had again to lie in the region where $\frac{d^2\psi}{dv^2}=0$ is negative above $T=T_1$. But a second case is possible.

With constantly rising temperature the intersection of the two curves may always proceed in the same sense, and then there can also be contact at $T=T_1$. Then the curve $\frac{d^2\psi}{dx^2}=0$ must disappear in the region where $\frac{d^2\psi}{dv^2}$ is positive. In Contribution III I gave the equation which is to decide whether $\frac{d^2\psi}{dx^2}=0$ is to disappear in the one region or in the other, viz.:

$$\frac{\alpha x_g(1-x_g)}{a} \gtrless \frac{4y_g^2}{1+y_g}.$$

If the sign $>$ holds, $\frac{d^2\psi}{dx^2}=0$ disappears in the region where $\frac{d^2\psi}{dv^2}$ is positive, and the other way about. And now, to answer the question whether the first mentioned case takes place or the second, we must examine this equation, bearing in mind that ε_1 and ε_2 is positive, and that the points $(\varepsilon_1, \varepsilon_2)$ lie below the parabola OPQ.

The values of x_g and y_g are dependent on n, and quite determined by this quantity; and according to the list of calculated values occurring in the beginning of Contribution III, x_g can only vary between $^1/_2$ and $^1/_3$, and y_g between $^1/_2$ and 0. So the second member of the inequality to be investigated is entirely determined by the ratio of the size of the molecules, but the first member depends moreover on ε_1 and ε_2.

Let us write this first member, omitting the index to x_g:

$$\frac{cx(1-x)}{a}=\frac{cx(1-x)}{a_1(1-x)+a_2x-cx(1-x)}=$$

$$\frac{1}{\frac{a_1}{c}\frac{1}{x}+\frac{a_2}{c}\frac{1}{1-x}-1}=\frac{1}{\frac{1+\varepsilon_1}{(n-1)^2}\frac{1}{x}+\frac{n^2(1+\varepsilon_2)}{(n-1)^2(1-x)}-1}$$

or

$$\frac{cx(1-x)}{a}=\frac{1}{\frac{1}{(n-1)^2}\frac{1}{x}+\frac{n^2}{(n-1)^2}\frac{1}{1-x}+\left[\frac{\varepsilon_1}{(n-1)^2}\frac{1}{x}+\frac{n^2\varepsilon_2}{(n-1)^2}\frac{1}{1-x}-1\right]}.$$

Now there is a series of values of ε_1 and ε_2 (see p. 483) for which the value of $\frac{\varepsilon_1}{(n-1)^2}\frac{1}{x}+\frac{n^2\varepsilon_2}{(n-1)^2}\frac{1}{1-x}-1$ is equal to 0. All these values are given by a line which touches the parabola in a point for which $\frac{\sqrt{\varepsilon_1}}{n-1}=x$, so a point which, as the parabola itself, is entirely determined by the value of n, and lies on the line which passes through the origin in a direction $\frac{\varepsilon_1}{\varepsilon_2}=n^2\left(\frac{x}{1-x}\right)^2$. This direction approaches to $\frac{n^2}{4}$ for very great values of n, and to n^2 itself for values of x which are but little greater than ½. All the values of ε_1 and ε_2 occurring below the parabola are reached when lines are traced parallel to the said tangent. Thus:

$$\frac{\varepsilon_1}{(n-1)^2}\frac{1}{x}+\frac{n^2\varepsilon_2}{(n-1)^2}\frac{1}{1-x}-1=\pm\,a$$

represents all the points below this tangent, when a is given the negative sign; and then the second member can descend to -1, in which case the origin itself might occur. All the points above the said tangent are reached, when a is given the positive sign, and then made to ascend till $1+a=\frac{1}{x}$, in which case the point Q is reached. For a such that $1+a=\frac{1}{1-x}$, the point P is reached.

So we have for points below the tangent:

$$\frac{cx\,(1-x)}{a}=\frac{1}{\frac{1}{(n-1)^2}\frac{1}{x}+\frac{n^2}{(n-1)^2}\frac{1}{1-x}-a},$$

in which a lies between 0 and 1, and is $=0$ on the tangent itself.

For points above the tangent we have:

$$\frac{cx\,(1-x)}{a}=\frac{1}{\frac{1}{(n-1)^2}\frac{1}{x}+\frac{n^2}{(n-1)^2}\frac{1}{1-x}+a},$$

in which a lies between 0 and $\frac{1}{x}-1$; whereas to reach the points lying above the tangent on the side of P we need not go further than $a=\frac{1}{1-x}-1$. Of course in the same way as illustrated in an example above we have again to consider whether all these points points probably occur by investigating the value of l^2.

The form in which $\frac{cx\,(1-x)}{a}$ has been given, now consists of two parts in the denominator. The first part $\frac{1}{(n-1)^2}\frac{1}{x}+\frac{n^2}{(n-1)^2}\frac{1}{1-x}$ depends only on n, but the second part a depends also on ε_1 and ε_2, and as the second member of the inequality which is to be investigated, does depend only on n, we cannot expect the circumstance whether $\frac{d^2\psi}{dx_2}=0$, when disappearing, lies in the positive region of $\frac{d^2\psi}{dv^2}$ or in the negative one, only to depend on the ratio of the size of the molecules. But this we may at once consider as a result obtained that as the parallel line is farther from the origin, and so the values of ε_1 and ε_2 are larger, the value of the first member of the inequality becomes smaller, and so there is a greater chance that the second member exceeds the first. For greater values of ε_1 and ε_2 there is a greater chance that the disappearance of $\frac{d^2\psi}{dx^2}=0$ takes place in the region where $\frac{d^2\psi}{dv^2}<0$, and the degree of the non-miscibility will be limited. Or rather, a phenomenon that attends non-miscibility, will be checked by this. Thus for $n=\infty$, for which $x=\frac{1}{3}$, and $y=\frac{1}{2}$, and $\frac{n}{n-1}=1$, the first member of the inequality will be equal to 2 for the origin, to $\frac{2}{3}$ for the points of the tangent mentioned, and $\frac{1}{2}$ for the point P if we include also the lefthand part above the tangent in our calculation; the second member is equal to $\frac{2}{3}$. Then $\frac{d^2\psi}{dx^2}=0$ disappears just on the verge of the region of $\frac{d^2\psi}{dv^2}$ positive or negative for the points of the tangent. For the points above the tangent, however, $\frac{d^2\psi}{dv^2} = 0$ disappears where $\frac{d^2\psi}{dv^2}$ is negative, and the reverse for the points below the tangent.

But let us try to answer the question where $\frac{d^2\psi}{dx^2} = 0$ disappears for arbitrary value of n. The relation between n, x, and y (Contribution III) is, indeed, a very intricate one — but to my astonishment it proved to be possible to find an answer by a comparatively simple reduction. If we start from equation (4) of Contribution III, we may write:

$$\frac{1}{n-1} + x = \frac{x(1-x)}{1-2x}\{1-y\}$$

and

$$\frac{n}{n-1} - (1-x) = \frac{x(1-x)}{1-2x}\{1-y\}$$

If we take the square of the first of these equations, and then divide by x — and the square of the second of these equations and then divide by $1-x$, the sum of the two values obtained yields:

$$\frac{1}{x}\frac{1}{(n-1)^2} + \frac{1}{1-x}\frac{n^2}{(n-1)^2} - 1 = \frac{x(1-x)}{(1-2x)^2}(1-y)^2$$

For the second member may also be written $\frac{1}{4}\frac{(1-y)^2}{y^2}$, and the condition whether $\frac{d^2\psi}{dv^2}$ is positive or negative for the point in which $\frac{d^2\psi}{dx^2} = 0$ disappears, becomes then for the points below the tangent:

$$\frac{1}{1 - a + \frac{1}{4}\frac{(1-y)^2}{y^2}} \gtrless \frac{4y^2}{1+y}$$

In this equation we have $a = 1$ for the origin and $a = 0$ for the tangent itself. With $a = 1$ we find as condition:

$$y(1+y) \gtrless (1-y)^2$$

For $y = \frac{1}{2}$, which belongs to $n = \infty$, the first member of the inequality is $\frac{3}{4}$, and the second member $\frac{1}{4}$. So, as we found above,

$\frac{d^2\psi}{dv^2} > 0$. But for $y = 0$, which would belong to $n = 1$, the first member $= 0$ and the second $= 1$. So for this limiting case $\frac{d^2\psi}{dv^2} < 0$. So there is a transition value of n, namely for that which belongs to $3y = 1$ or $y = \frac{1}{3}$. According to Contribution III the value of x is about 0.41 and of n about 3.4 for this value of y.

For the points of the tangent for which $a = 0$, the condition is:

$$\frac{1}{1 + \frac{1}{4}\frac{(1-y)^2}{y^2}} \gtrless \frac{4y^2}{1+y}$$

or

$$0 \gtrless 4y^3 - 3y + 1$$

or

$$0 \gtrless (1 - 2y)^2 (1 + y).$$

So this inequality can never be satisfied by the sign $>$; only for $y = \frac{1}{2}$ there is equality, as we saw already above. We conclude from this that however great the value of n be, $\frac{d^2\psi}{dx^2} = 0$ disappears in the region where $\frac{d^2\psi}{dv^2}$ is negative for all the points of the tangents. So this is a fortiori the case for all the points above the tangent. When y lies between $\frac{1}{3}$ and $\frac{1}{2}$, and so $n > 3.4$, a line is to be indicated parallel to the tangent on which the points $(\varepsilon_1, \varepsilon_2)$ must lie for $\frac{d^2\psi}{dx^2} = 0$ to disappear, just on the verge of $\frac{d^2\psi}{dv^2} = 0$. But for values of $y < \frac{1}{3}$ and $n < 3.4$ the disappearance will take place where $\frac{d^2\psi}{dv^2}$ is negative for all the points below the parabola, and so the curve $\frac{d^2\psi}{dv_2} = 0$ will lie inside the curve $\frac{d^2\psi}{dv^2} = 0$ both at a temperature below T_1, so before the first contact, and at a temperature above T_2, so after the second contact. The place of the straight line which contains the points at which the transition of the sign of

$\frac{d^2\psi}{dv^2}$ takes place is determined by the value of $\alpha = 1 - \frac{3y-1}{4y^3}$ or $\alpha = \frac{(2y-1)^2(1+y)}{4y^3}$. So the quantity α has always the same sign, and as it cannot be greater than 1, y must always be greater than $\frac{1}{3}$. So the equation of this line is:

$$\frac{\varepsilon_1}{(n-1)^2}\frac{1}{x} + \frac{n^2\varepsilon_2}{(n-1)^2}\frac{1}{1-x} = \frac{3y-1}{4y^3}$$

Now we have also the means to decide whether the temperature at which $\frac{d^2\psi}{dx^2} = 0$ disappears, is higher or lower than the critical temperature of the mixture of the value of $x = x_g$ — in other words whether $T_g \gtrless T_k$. If $T_g < T_k$, then $\frac{d^2\psi}{dx^2} = 0$ has left the region where $\frac{d^2\psi}{dv^2} < 0$ on the side of the branch of the small volumes of $\frac{d^2\psi}{dv^2} = 0$, and this branch is still found even at the temperature T_g. For the other case we have a representation of the relative position of the two curves after they had left each other in fig. 10, Contribution III. The condition $T_g \gtrless T_k$ (see Contribution III) may be written:

$$\frac{2c}{b}x(1-x)\frac{1-y}{(1+y)^2} \gtrless \frac{8}{27}\frac{a}{b}$$

or

$$\frac{27}{4}\frac{cx(1-x)}{a} \gtrless \frac{(1+y)^2}{(1-y)}.$$

If we write further $\frac{cx(1-x)}{a} = \frac{1}{1-\alpha+\frac{(1-y)^2}{4y^3}}$, the condition becomes:

$$\frac{27}{4}\frac{1}{1-\alpha+\frac{(1-y)^2}{4y^3}} \gtrless \frac{(1+y)^2}{1-y}$$

For $\alpha = 1$, or for the origin O, this condition becomes:

$$27\,y^3 \gtrless (1+y)^2(1-y).$$

For $y = \frac{1}{2}$ or $n = \infty$ the first member of the inequality becomes equal to $\frac{27}{8}$, and the second member to $\frac{9}{8}$; which means that

$T_g = 3T_k$. But for $y=0$ or $n=1$ the first member $=0$, and the second $=1$. So there is a value of y, for which $T_g = T_k$, and of course this value must be larger than that which we found above, when we determined for what value of y the curve $\frac{d^2\psi}{dx^2}$ disappears on the boundary of $\frac{d^2\psi}{dv^2}=0$. So if we put $y=\frac{1}{3}$ the first member is equal to 1, and the second to $\frac{32}{27}$. The equality of the two members requires y about 0,36, to which $n=3.7$ corresponds, which is but little greater than we found above for the smallest value of n for which $\frac{d^2\psi}{dx^2}=0$ goes beyond $\frac{d^2\psi}{dv^2}=0$.

For the tangent for which $\alpha=0$, the condition becomes:

$$\frac{27}{4}\,\frac{1}{1+\dfrac{(1-4)^2}{4y^2}} \gtrless \frac{(1+y)^2}{(1-y)}$$

We cannot expect another value for the points of the tangent than $y=\frac{1}{2}$. The last inequality may also be written:

$$0 \gtrless (1-2y)^2\,(1+4y+10y^2+y^3).$$

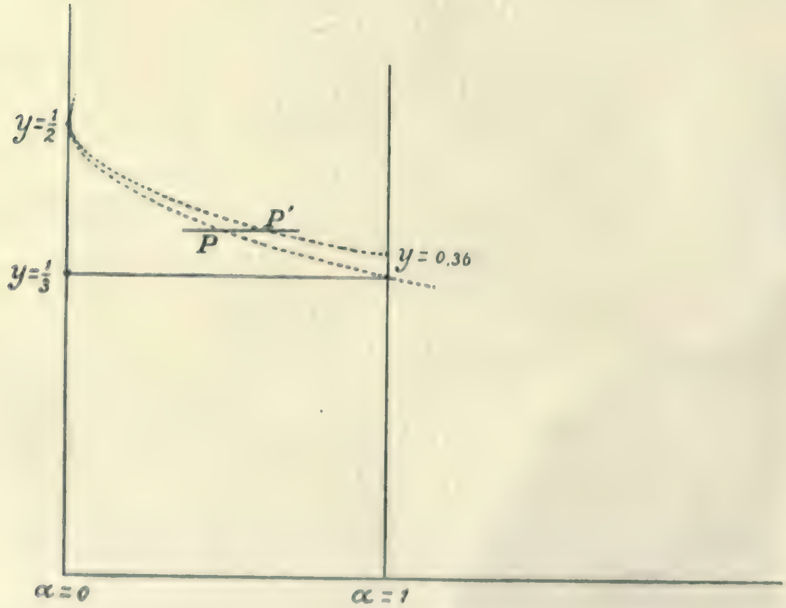


Fig. 38

If we call the value of α required to change the inequality into equality for given value of y, α' — then the relation:

$$1-\alpha'=\frac{27}{4}\frac{1-y}{(1+y)^2}-\frac{(1-y)^2}{4y^3},$$

holds for this quantity.

For the preceding problem, viz. the determination of the relation between α and y causing $\frac{d^2\psi}{dx^2}=0$ to disappear on the curve $\frac{d^2\psi}{dv^2}=0$,

$$1-\alpha=\frac{3y-1}{4y^3}$$

held.

For $\alpha'-\alpha$ we find then:

$$\alpha'-\alpha=\frac{1+y}{4y^2}-\frac{27}{4}\frac{1-y}{(1+y)^2}$$

or

$$\alpha'-\alpha=\frac{(1+y)^3-27\,y^2\,(1-y)}{4y^2\,(1+y)^2}=\frac{(1-2y)^2\,(1+7y)}{4y^2\,(1+y)^2}.$$

From this it appears, what had been clear beforehand, that α' is always greater than α, except for $y=\frac{1}{2}$, when they are both equal to 0, and so for the points of the tangent. A case, however, which we can only think as a limiting case, because it would require $n=\infty$. The adjoined figure 38 gives the relation between α and y for the two problems graphically. For the origin $\alpha=1$, and for the points of the tangent $\alpha=0$. For the first problem $y=\frac{1}{3}$ for the origin, and for the second $y=0{,}36$ — whereas for $\alpha=0$ the two values of y are $=\frac{1}{2}$. For the second problem the line $y=f(\alpha)$ always lies above that of the first problem. Hence for equal value of y the point P' lies at higher value of α than the point P.

(*To be continued*).

Anatomy. — *"About the development of the urogenital canal (urethra) in man."* By A. J. P. v. d. Broek. (Communicated by Prof. L. Bolk).

In the following communication I am going to give a description of the way in which ontogenetically the closure of the urogenital canal comes about in man; next I intend trying to throw some light upon the composition of this canal from a comparative point of view.

The youngest stage that I examined was a male (?) embryo of a length of 30 m.m. from crown to coccyx; a stage which is a little younger than the oldest female embryo (l.c. Embryo Lo) described by Keibel [1]).

The urodaeum (entodermal cloaca) is divided into rectum and sinus urogenitalis; there is a primitive perinaeum. The anal membrane no longer lies near the surface of the body, but forms the bottom of a short proctodaeum. Sinus urogenitalis and proctodaeum combine into a short (200 μ) ectodaeum (ectodermal cloaca), in whose walls the two component parts are easy to recognize. If we follow the part of the wall proceeding from the sinus urogenitalis, it appears that this at the basis of the penis contributes to the limitation of the short genital groove ("Geschlechtsrinne"); before this it continues in the beginning of the penis as an epithelial double lamella, phallusframe ("Urogenitalplatte", "Urethralplatte", "lame cloacale" etc.). There is not yet a fossa navicularis.

In an embryo of 4 c.m. the apertures of proctodaeum (anus) and sinus urogenitalis are separated by a definitive perinaeum.

The sinus urogenitalis mouths on the perineal penis-surface with an aperture about lozenge-shaped, situated immediately behind a circular furrow on the penis. This furrow denotes the limit between the glans and the corpus of the penis.

Following the transverse sections, starting from the apex of the penis, it appears how in the part before the navicular aperture (fossa navicularis) the phallus-frame as double-lamella penetrates into the tissue of the penis (fig. 1 a). In the sphere of the fossa navicularis the lamellae of the phallus-frame partly deviate (fig. 1. b.), by which on the perineal surface a groove becomes visible. The angle between the two leaves becomes gradually larger, till at last, in the widest part of the aperture, one is the continuation of the other (figure 1 c. and d.). The upper part of the phallus frame stands like a crest upon the cornerplace of the deviating lamellae. (fig. 1 b-d.).

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[1]) Keibel (F.). Zur Entwickelungsgeschichte des menschlichen Urogenitalapparates. Archiv f. Anatomie und Physiologie. Anat. Abth. 1896. pag. 55.

If we look more closely at the wall of the fossa navicularis, it appears that it is only partially formed by the lamellae of the phallus-frame; the rest originates from the penisectoderm, which by the side of the phallus-frame bends like a fold over its edge (marked in fig. 1 b and c. with g.p.). If this fold is to be called sexual-fold, it must be borne in mind that it does not represent the transition-edge of the phallus-frame into the penisectoderm, but entirely originates from this ectoderm. In figure 1 b the two sexual folds are situated close to each other, in figure 1 c, corresponding to the middle of the fossa navicularis they are farther distant.

Towards the base of the penis the two lamellae of the phallus-frame remain each other's continuation; likewise the median crest remains present; the two sexual folds, on the other hand, keep bending to one another till they reach each other in the median line and close the urogenital canal. Accordingly the wall of this canal consists of two parts, originating from the phallus-frame and from the sexual folds (penisectoderm) (fig. 1 d.). At the nature of the epithelium they are to be recognized microscopically.

In the discussion of the older embryos I shall restrict myself to that place, where comes about the closure of the urogenital canal. I mention in passing that the part already closed, grows in length during the following time of development and contributes to the growth of the perinaeum.

In an embryo of 5 cm. the place where the two sexual folds meet in the median line, is situated somewhat behind the broadest part of the fossa navicularis. Here, too, the two wall-parts of the urogenital canal, originating from the phallus-frame and from the sexual folds are clearly to be distinguished from each other. The part of the phallus-frame not separated lies like a crest on the ventral wall of the urogenital canal; before the fossa navicularis the phallus-frame forms an epithelial double-lamella. In this embryo a praeputium has appeared which has not yet entirely grown about the penis. The closure of the urogenital canal now goes on in apical direction, so that the orificum externum urethrae is removed to the point of the penis. This removal runs almost parallel to the growing of the praeputium round the glans penis.

In the closed part of the urogenital canal the wall every time consists of the two parts described higher up, which are microscopically sharply to be distinguished. Differences appear only in the proportions in which the two epithelia contribute in the formation of the wall. In an embryo of a length of 8.5 cm the praeputium has grown round the whole glans. The orificium externum urethrae finds itself not far behind the apex of the penis on the perineal surface of the glans.

The first sections, beginning at the apex of the penis, still show the solid phallus-frame (fig. 2 a.). The aperture of the urogenital canal is to be seen in fig. 2 a as a groove in the thick mass of epithelium, having arisen by the meeting of the two edges of the praeputium. Through this the urogenital canal runs in an oblique direction and after some sections it reaches the surface of the glans. In that place the two lamellae of the phallus-frame have partly deviated a little from each other (fig. 2 b.). The adjoining penisectoderm forms at the edges of the phallus-frame two small sexual folds (marked in fig. 2 b with *g p*). By the meeting of these two folds, some sections further on, the closure of the urogenital canal is brought about (fig. 2 c). In contradistinction to what we saw in the sphere of the fossa navicularis, the phallus-frame has by far the greatest part in the formation of the wall of the urethra; only a very small part proceeds from the sexual folds (penisectoderm).

That here, also, the two wall-parts are easy to distinguish from each other, is taught by fig. 3, in which a part of fig. 2*c* under high power is sketched.

The epithelium of the phallus-frame is to be recognized in a very distinct stratum germinativum of high cylindrical cells; between the stratum germinativum on either side there are a number of big, little coloured, polygonal cells with large round nuclei. The cell-boundaries are very clear. The groove between the deviated parts of the phallus-frame possesses a smooth surface.

The epithelium proceeding from the penisectoderm and covering the foremost part of the canal, has quite a different appearance.

It has a much darker colour, probably partially a consequence of the much closer arrangement of the nuclei. A clear stratum germinativum is not to be recognized, no more are the cell-boundaries visible; the limitation of the lumen is not so smooth and sharp as in the phallus-frame.

If we follow the urethra towards the fossa navicularis, we see two kinds of changes taking place. First in the wall-formation a place getting larger and larger is given to the penisectoderm; secondly the two lamellae of the phallus-frame deviate more and more, only a small part remaining in the shape of a crest on the urethra (fig. 2*e*). The epithelium of the phallus-frame is gradually replaced by an epithelium having the character of the penisectoderm. In the section from which fig. 2*g* has been borrowed, the two components which are ontogenetically contained in it, are no more to be recognized. I cannot omit directing attention in this figure to the epithelial knob lying dorsally with respect to the urethra. It represents the "Anlage" of one of the so-called para-urethralpassages and is to be considered as a separated part of the phallus-frame or as a cell-cord grown inside from this frame.

Finally I give in fig. 4 a series of sections through the urethra of an embryo 13 cm. long (± at the end of the 5th month) in which embryo the state of the full-grown man has been reached.

The urethra mouths at the end of the penis with a vertical aperture. Where the urethra is vertical, accordingly before the fossa navicularis, its wall, as is shown in fig. 4*a*, consists principally of the epithelium of the phallus-frame; only an exceedingly small part proceeds from the penisectoderm, resp. the sexual folds. The lamellae of the phallus-frame are almost entirely separated, not because they are deviated, but because the central mass has disappeared.

In the direction to the fossa navicularis also here the composition of the wall changes and the part proceeding from the phallus-frame becomes smaller, the part originating from the sexual folds becomes larger. In fig. 4 c the vertical part of the canal certainly answers to the phallus-frame, the rest is for the greater part a production of the sexual folds. Also in this preparation the difference between the two kinds of epithelium disappears in the sphere of the fossa navicularis; in the sections from which fig. 4 d-g has been borrowed the boundaries between the two components are no more to be seen.

In different places separated cell-cords and tubes are present which must be considered as the "Anlages" of paraurethralpassages; the tube in fig. 4*f* marked *s. g.* is the "Anlage" of the sinus of Guérin.

The series fig. 4, like fig. 2, shows the cause of the change in the position of the urethra, which, as is well-known, stands vertical before the fossa navicularis, behind it mostly horizontal. The difference is based upon the difference in composition. For before the fossa navicularis it is the phallus-frame, which has a vertical position, that forms the greatest part in the wall-formation of the urethra, only a small part proceeds from the sexual folds. Behind this fossa, on the other hand, the wall of the urethra is for the greater part the production of the united sexual folds, only a small part proceeding ontogenetically from the phallus-frame. The deviation of the two lamellae of the phallus-frame is in this transformation an important factor.

Considering the ontogenetical processes which contribute to the closure of the urogenital canal, as they have been described before, I have to join the group of investigators (RETTERER, REICHEL, HERZOG) who assume a closure in consequence of the combination of two folds (sexual folds) in the median line. I deviate from their opinion as to the origin of the sexual folds, which are not the edges of the phallus-frame, but which represent folds of the penisectoderm.

In connection with the processes described above I finally wish to give some ideas about the value and the importance of the urethra from a comparative ontogenetical point of view. For this purpose I have to remind of the state, as it occurs in Echidna, one of the Monotremata. In this animal, as KEIBEL'S [1]) investigation taught us, a couple of tubes, the so-called "Samenurethra" and the "Harnurethra" are developed caudally from the glands of Cowper. The former runs like a canal through the penis and is a production of the phallus-frame; the latter goes from the urogenital canal oblique caudally to the ectodaeum (ectodermal cloaca). Genetically this tube is formed, because the original single ectodaeum is divided by means of two folds which come together and unite, into two halves, the proctodaeum and the "Harnurethra". For the group of the Marsupialia I [2]) have proved that the urogenital canal must not be considered as a homologon to the "Samenurethra" of Echidna (as is generally done for the urethra of placental mammals on the ground of its topography with respect to the corpus cavernosum), but that it must be considered as a combination-product of "Samenurethra" and "Harnurethra", which placed themselves against each other and formed one canal. In Perameles there exists a transition between Echidna and placental mammals (man).

Applying the explanation given for the marsupialia about the genetical composition of the urogenital canal to the urethra of man, I come to the conclusion that here, too, a real "Samenharnurethra" exists, homologous to the "Samenurethra" + "Harnurethra" of Echidna. To be compared with the "Samenurethra" is that part of the urethra which owes its origin to the phallus-frame. The homologa of the two folds of the ectodaeum are the two folds which I described as sexual folds, by whose meeting the closure of the urogenital canal is brought about. The part bounded by these folds thereby becomes homologous to the "Harnurethra."

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[1]) KEIBEL (F.). Zur Entwickelungsgeschichte des Urogenitalapparates von Echidna aculeata var. typica. Semon. zoöl. Forschungsreisen. Lieferung 22. pg. 153—206.

[2]) v. D. BROEK (A. J. P.) Zur Entwickelungsgeschichte des Urogenitalkanales bei Beutlern. Verhandl. der Anat. Gesellschaft. 22. Berlin 1908, pg. 104—120.

From a comparative ontogenetical point of view, therefore, also the value of the urethra before and behind the fossa navicularis is different. For, whereas behind the fossa navicularis only a very small portion of the wall can be considered as a production of the phallus-frame, perhaps the vertical part of the lumen as it is found in the urethra of man, this changes before the fossa navicularis in such a way that there the greater part of the wall originates from that frame; therefore behind this fossa the urethra is principally homologous to the "Harnurethra", before it to the "Samenurethra".

Mathematics. — "*On bicuspidal curves of order four.*" By Prof. JAN DE VRIES.

1. It is easy to see, that each curve of order four, C_4, with two cusps can be represented by the equation

$$x_1^2x_2^2 + 2x_1x_2x_3^2 + 2b_1x_1x_3^3 + 2b_2x_2x_3^3 + cx_3^4 = 0.$$

The triangle of reference has then the cusps O_1, O_2 and the point of intersection O_3 of the cuspidal tangents as vertices.

From the equation

$$(x_1x_2 + x_3^2)^2 + 2(b_1x_1 + b_2x_2 + b_3x_3)\, x_3^3 = 0,$$

where $2b_3 = c - 1$, is evident that

$$b_x \equiv b_1x_1 + b_2x_2 + b_3x_3 = 0$$

represents the *double tangent* d of C_4 and that the conic

$$u \equiv x_1x_2 + x_3^2 = 0$$

passes through the tangential points D_1, D_2 of d and *osculates* C_4 in the cusps O_1 and O_2.

By combining the equations

$$u^2 + 2b_xx_3^3 = 0 \quad \text{and} \quad u = \lambda b_xx_3$$

we understand that the conics A_2 through O_1, O_2, D_1 and D_2 generate a system of pairs of points on C_4, which are lying in pairs on the rays

$$2x_3 + \lambda^2 b_x = 0$$

of the pencil, having the point of intersection H of $k \equiv O_1O_2$ and d as vertex.

As this system of points with the curve is given we shall denote it as the *fundamental involution* F_2.

If we put $\lambda^2 = \mu$, it follows from

$$2x_3 + \mu b_x = 0 \quad , \quad u^2 = \mu b_x^2 x_3^2 \, ,$$

that C_4 can be generated by a pencil of conics $(O_1O_2D_1D_2)$ arranged in the pairs of an involution and a pencil of lines (H) between which such a projective relation exists that the rays d and k through H correspond to the double-elements of the involution, the first of which is composed of the right lines d and k. The locus of the points of intersection of corresponding elements thus consists of the line d and a C_4 with cusps O_1, O_2.

The polar line h of point $H(b_2, -b_1, 0)$ with respect to the conic A_2,

$$x_1x_2 + x_3^2 = \lambda(b_1x_1 + b_2x_2 + b_3x_3)\,x_3,$$

has as equation $b_2(x_2 - \lambda b_1x_3) - b_1(x_1 - \lambda b_2x_3) = 0$ or

$$b_1x_1 = b_2x_2.$$

On the line h lie the points Q_1, Q_2, which are connected with the pair of points P_1, P_2 of F_2 generated by A_2 in such a way that we have

$$Q_1 \equiv (O_1P_1, O_2P_2) \text{ and } Q_2 \equiv (O_1P_2, O_2P_1).$$

The fundamental involution F_2 is thus projected out of O_1 and out of O_2 in the same involutory system of points (Q_1, Q_2). Now Q_1 is the projection of *two* points P_1 and P_1' of C_4, so it is conjugate to two points, Q_2 and Q_2', by means of F_2. Therefore the pairs Q_1, Q_2 form on h an involutory correspondence (2,2).

2. The points of C_4 are projected out of O_1 and O_2 by two pencils in correspondence (2,2); the line k is for both systems a branch-ray, because it is conjugate to the two cuspidal tangents k_1 and k_2; the remaining branch-rays are the tangents out of O_1 and O_2 to C_4.

These tangents are represented by

$$2b_1x_1^3 + 2b_2x_1^2x_3 - 2b_2x_1x_3^2 - b_2^2x_3^3 = 0,$$
$$2b_2x_2^3 + 2b_3x_2^2x_3 - 2b_1x_2x_3^2 - b_1^2x_3^3 = 0.$$

Through the points of intersection of these two three-rays passes the figure, represented by

$$(b_1^3x_1^3 - b_2^3x_2^3) + b_3x_3(b_1^2x_1^2 - b_2^2x_2^2) - b_1b_2x_3^2(b_1x_1 - b_2x_2) = 0.$$

It is composed of the line h,

$$b_1x_1 = b_2x_2,$$

and the conic

$$(b_1x_1 + b_2x_2)\,b_x - b_1b_2(x_1x_2 + x_3^2) = 0.$$

The tangents r_1, s_1, t_1 out of O_1 can thus be conjugated to the tangents r_2, s_2, t_2 out of O_2 in such a way that the points of intersection $R \equiv r_1r_2$, $S \equiv s_1s_2$, $T \equiv t_1t_2$ lie with the point of intersection of the cuspidal tangents on a right line h.

At the same time a new proof has been given for the well-known property [1], according to which the singular elements (branch-elements and double-elements conjugate to them) of a correspondence (2,2) can be arranged in such a way that the singular elements of the first system correspond projectively to those of the second one.

For, if two pencils are connected by a (2, 2) we have but to rotate them around their vertices until a branch-ray of the first pencil coincides with a branch-ray of the second; in the new position they then generate a C_4 with two cusps. From this is evident that there are four projectivities between the singular elements [2].

The (2 , 2) between the pencils $x_1 = \lambda x_3$ and $x_2 = \mu x_3$ has as equation

$$\lambda^2\mu^2 + 2\lambda\mu + 2b_1\lambda + 2b_2\mu + c = 0.$$

By the points of h these pencils are arranged in the projectivity

$$b_1\lambda = b_2\mu'$$

By eliminating λ we find out of these two relations the equation of the correspondence (2 , 2) between the points which conjugate rays of the pencils (O_1) and (O_2) generate on h. And now it is evident from

$$b^2_2\,\mu^2\,\mu'^2 + 2b_1\,b_2\,\mu\mu' + 2b_1^2\,b_2\,(\mu + \mu') + b_1^2\,c = 0$$

that this correspondence is involutory.

This result is in accordance with the well-known property [3], according to which a (2 , 2) between two collocal systems is involutory when the two systems have the same branch-elements.

3. Evidently the involutory (2, 2) on h does not differ from the (2, 2) which was deduced from the fundamental involution F_2. Its coincidences arise from the four tangents which one can draw from H to C_4. Indeed, *the polarcurve of H consists of the line h and the conic u* (passing through the points of contact of d).

If the branch-point $R = r_1r_2$ is conjugate to the double-point R', then R' must be the point of intersection of the rays which the points of contact R_1 and R_2 of r_1 and r_2 project out of O_2 and O_1.

We conclude from this that *the tangential points R_1, S_1 T_1 of the*

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[1] Emil Weyr, *Beiträge zur Curvenlehre*, Vienna 1880, Alfred Hölder, p. 32, or *Annali di Matematica*, 1871, IV, p. 272.

[2] In my paper "*Over vlakke krommen van de vierde orde met twee dubbelpunten*" (N. Archief voor Wiskunde, 1888, XIV, p. 193) I have applied the properties of the (2,2) correspondence to those curves.

[3] Emil Weyr „*Ueber einen Correspondenzsatz*", Sitz. ber. der K. Akad. in Wien, 1883, LXXXVII, p. 595, or my paper under the same title in N. Archief voor Wiskunde, 1907, VII, p. 469.

tangents r_1, s_1, t_1 *are projected out of the point* H *into the tangential points* R_2, S_2, T_2 *of the tangents* r_2, s_2, t_2.

If S' corresponds as a double-point of the (2, 2) to $S \equiv s_1 s_2$, then it follows from

$O_1(RR'SS') = O_2(RR'SS')$, that we have $O_1(RR'SS') = O_2(R'RS'S)$.

From this follows that *the points* R_1, R_2, S_1, S_2 *are connected with* O_1, O_2 *by a conic.* Also the groups $O_1, O_2, R_1, R_2, T_1, T_2$ and $O_1, O_2, S_1, S_2, T_1, T_2$ lie on conics.

If $K \equiv hk$ we find out of

$$O_1\,(O_3\,KRR') = O_2\,(O_3\,K'RR') = O_2\,(K'O_3\,R'R),$$

that through R_1 and R_2 passes a conic which is touched in O_1 and O_2 by the cuspidal tangents. The pairs of points S_1, S_2 and T_1, T_2. procure two analogous conics.

If two arbitrary points X and Y of h are projected out of O_1 and O_2, then the points (O_1X, O_2Y) and (O_1Y, O_2X) lie in a right line through H.

From this follows that H bears three right lines which contain successively the pairs of points

$$\begin{array}{lll} 1 \equiv r_1 s_2 \\ 4 \equiv r_2 s_1 \end{array}\Bigg\} \quad \begin{array}{l} 2 \equiv r_1 t_2 \\ 5 \equiv r_2 t_1 \end{array}\Bigg\} \quad \begin{array}{l} 3 \equiv s_1 t_2 \\ 6 \equiv s_2 t_1 \end{array}\Bigg\}$$

Above we found that these six points lie on a conic and form two hexagons having O_1 and O_2 as point of Brianchon: it is now evident that they determine a third hexagon, having H as point of Brianchon.

4. From $(kr_1\,s_1\,t_1) = (kr_2\,s_2\,t_2)$ follows

$$(kr_1 s_1 t_1) = (r_2 k t_2 s_2) = (s_2 t_2 k r_2) = (t_2 s_2 r_2 k).$$

So we can bring through O_1 and O_2 three conics $\varrho_2, \sigma_2, \tau_2$ with respect to which the line k has as poles the points R, S, T, whilst containing successively the pairs of points 3,6; 2,5 and 1,4.

On these three conics the pencils (O_1) and (O_2), arranged in (2,2) determine, just as on h, involutory correspondences (2,2); for, the two systems of points generated on them have again the branch-points in common.

If M_1, M_2 is a pair of the (2,2) determined on ϱ_2, then the points (O_1M_1, O_2M_2) and (O_1M_2, O_2M_1) lie on C_4 and in *one* line with the point R, namely on the polar line of the point (M_1M_2, O_1O_2) with respect to ϱ_2.

The pencils with vertices R, S and T generate therefore on C_4 *three more fundamental involutions of pairs of points* where again each ray contains two pairs. They differ from F_2 in this, that unlike the former they do not contain the tangential points of the double tangent as a pair.

For $M_1 \equiv M_2$ we have a coincidence of the (2,2). From this is evident that the tangential points of the four tangents which can still be drawn from R, S or T to C_4, are every time connected with O_1 and O_2 by a conic $(\varrho_2, \sigma_2, \tau_2)$.

In an analogous way as for F_2 we find by paying attention to the singular elements of the (2, 2) on ϱ_2, σ_2 and τ_2, that *the lines S_1T_2 and S_2T_1 concur in R, the lines R_1T_2 and R_2T_1 in S the lines R_1S_2 and R_2S_1 in T.*

5. The polarcurve of the point $(y_1, y_2, 0)$ has as equation

$$y_1(x_1x_2^2 + x_2x_3^2 + b_1x_3^3) + y_2(x_1^2x_2 + x_1x_3^2 + b_2x_3^3) = 0,$$

or

$$(y_2x_1 + y_1x_2)(x_1x_2 + x_3^2) + (b_1y_1 + b_2y_2)\,x_3^3 = 0.$$

By combination with the equation

$$(x_1x_2 + x_3^2)^2 + 2b_xx_3^3 = 0$$

of the C_4 is evident that the points of intersection of the two curves lie on $x_1x_2 + x_3^2 = 0$ and on the curve

$$2(y_2x_1 + y_1x_2)\,b_x = (b_1y_1 + b_2y_2)(x_1x_2 + x_3^2).$$

Therefore the tangential points of the tangents out of a point of O_1O_2 lie on a conic η_2.

For $y_1 : y_2 = b_2 : b_1$, i.e. the point $K = hk$, we find the conic $(b_1x_1 + b_2x_2)\,b_x = b_1b_2(x_1x_2 + x_3^2)$ through the points 1,2,3,4,5,6.

Out of the equation

$$y_1\{b_1(x_1x_2 + x_3^2) - 2x_2b_x\} + y_2\{b_2(x_1x_2 + x_3^2) - 2x_1b_x\} = 0$$

is evident that the conics η_2 form a pencil having as basis the points of intersection of $x_1x_2 + x_3^2 = 0$ with $b_x = 0$ (the points D_1, D_2) and two points of $b_1x_1 = b_2x_2$ (the line h).

One of the pairs of lines consists of the lines d and h; it contains the tangential points of the tangents out of H, two of which are united in d.

The other two pairs of lines belong to two points of O_1O_2, for which the six tangential points lie every time on two lines passing through D_1 and D_2.

6. If (y_k) is a point of d, thus $b_y = 0$, then its polar curve with respect to C_4 is represented by

$$2(y_1x_2 + y_2x_1 + 2y_3x_3)(x_1x_2 + x_3^2) + 6y_3x_3^2b_x = 0.$$

The points of intersection of these curve with C_4 which are not situated at the same time on $x_1x_2 + x_3^2 = 0$ lie on the conic ξ_2,

$$3y_3 (x_1x_3 + x_2^2) = 2 (y_2x_1 + y_1x_2 + 2y_3x_3)\, x_3 .$$

So the tangential points of the four tangents out of any point of the double tangent lie on a conic through the cusps.

For $y_3 = 0$, so $y_1 : y_2 = b_2 : - b_1$ (the point H) we find as it ought to be

$$(b_1x_1 - b_2x_2)\, x_3 = 0.$$

The conics ξ_2 form evidently a pencil of which two basepoints lie on h, the remaining two in O_1 and O_2.

7. The curve of Hesse of C_4 has as equation.

$$6x_1^3x_2^3 + 18 (b_1x_1 + b_2x_2)\, x_1^2x_2^2x_3 + (18c + 32)\, x_1^2x_2^2x_3^2 +$$
$$+ 60 (b_1x_1 + b_2x_2)\, x_1x_2x_3^3 + (36b_1b_2 + 24c - 8)\, x_1x_2x_3^4 +$$
$$+ 9 (b_1x_1 + b_2x_2)^2\, x_3^4 + 18 (b_1x_1 + b_2x_2)\, x_3^5 + (18b_1b_2 + c)\, x_3^6 = 0.$$

By combination with the equation of C_4 we find that the points of intersection of the two curves not lying in the cusps are situated on the curve

$$12 (b_1x_1 + b_2x_2)x_1x_2 + (18b_1b_2 - 18c - 30)x_1x_2x_3 - 27 (b_1x_1 + b_2x_2)^2x_3 -$$
$$- (54c + 22) (b_1x_1 + b_2x_2)x_3^2 + (18b_1b_2 - 19c - 18c^2)x_3^3 = 0.$$

So the eight points of inflexion of the C_4 are situated on a cubic curve passing through the cusps and the point H.

The polarcurve of the point $O_3 = k_1\, k_2$ consists of $x_3 = 0$ and the conic

$$2\, x_1x_2 + 3\, b_1x_1x_3 + 3\, b_2x_2x_3 + 2\, cx_3^2 = 0,$$

passing through the cusps and through the points of contact of the four tangents which meet in the point of concurrence of the cuspidal tangents.

It is easy to see that O_3 and H are the only points for which the polarcurve degenerates.

Chemistry. — "*On the system hydrogen bromide and bromine.*" By Dr. E. H. Büchner and Dr. B. J. Karsten. (Communicated by Prof. A. F. Holleman).

The research, a report of which is given here, was undertaken in connection with a remark from Prof. Holleman, that the existence of compounds of the type HBr_n has been assumed several times in order to explain the mechanism of reactions in organic chemistry. In order to test the validity of this assumption it was thought desirable to ascertain, in the first place, whether pure bromine and hydrogen bromide are capable of forming a compound. As in binary systems the safest conclusions as to the existence or non-existence of a compound may be drawn from the course of the melting point curves we have attempted to determine the melting point figure of the system HBr-Br.

It soon became evident that, at atmospheric pressure, the hydrogen bromide instantly escaped from the mixtures so that we were compelled to use sealed tubes. The experiments were now carried out as follows: A quantity of specially purified bromine was weighed in a glass tube a part of which was drawn out; the tube was now connected to a HBr-generating apparatus and placed in a bath of solid carbon dioxide and alcohol. As soon as a sufficient quantity of HBr had condensed the tube was sealed and reweighed. The hydrogen bromide which was prepared from bromine, phosphorus and water was dried by passing it through two U-tubes containing P_2O_5 whilst care was also taken that no moisture could enter the tube during the condensation. The tube was now fixed in a frame of copper wire and suspended in a rectangular wooden case, the long sides of which consisted of glass panes; in order to get a better isolation a second pane was fixed to each of these. Inside this case was placed a mixture of calcium chloride and ice for the higher temperatures whilst for the lower ones down to — 50° solid carbon dioxide and alcohol were used. For still lower temperatures this apparatus is unsuitable and the ordinary vacuum vessels were used; these, however, suffer from the disadvantage that, unlike in the other apparatus, the tubes cannot be shaken properly without lifting them out. Anyhow, in all cases we allowed the temperature of both to rise very slowly and the reading of the thermometer was taken at the moment that the last crystals fused. If only care be taken that the bath is kept constant at a trifling lower temperature for some time and that the tube and the bath are well stirred we may assume that the temperature of the mixture is practically the same as that of the bath. The observations were made with an "Anschütz" thermometer down to — 40° and a BAUDIN toluene thermometer for the lower temperatures; each determination was repeated a few times and the subjoined figures represent the mean result.

Before stating our results we just wish to explain, that, strictly speaking, we do not determine a melting point curve by means of the method described, for a vapour phase is also existent in the tubes which deviates considerably in composition from the liquid, and exists perhaps under a relatively high pressure. And from the weighings we know only the total concentration, and not that of the liquid phase alone. From some calculations, however, it appears that the composition of the liquid corresponds fairly well with the total-composition [1]), so that the curve representing our results graphically does not differ much from the projection on the *t*, *x*-plane of the liquid-branch of the three-phase line, when we call to mind the *p*, *t*, *x* model in space of BAKHUIS ROOZEBOOM. In any case, the conclusions as to the existence of compounds which we can draw from the course of the curve, remain unaltered.

In the subjoined table our figures are united whilst in the annexed drawing they are represented graphically; it should be observed that the composition is expressed in mol. percentage of Br_2.

Composition in mol. $^0/_0$ Br_2.	End melting point.	Initial melting point
0.0	— 87.3°	
1.2	— 88	— 94°
3.3	— 91	— 95
9.6	— 73.5	— 95.5
17.4	— 61.5	— 96
31.6	— 48	— 93
41.0	— 41.5	— 95
50.5	— 35.5	
55.8	— 32.5	
69.0	— 24.5	
77.6	— 19.6	
87.7	— 13.4	

The drawing, as will be noticed, does not leave the least doubt; bromine and hydrogen bromide do not form a single solid compound. It has not yet been decided whether the solid phases which are deposited, consist of pure bromine and pure hydrogen bromide or of mixed crystals; in the latter case there is a discontinuous series as at about —95° a eutectic point was observed.

Some experiments on the composition of the liquid and vapour phases at a pressure of one atm. render it highly probable that a compound of the type HBr_n does not occur in the liquid or the vapour. Moreover, the fact that in our tubes the pressure exceeded 1 atm. showed that at 1 atm. solid bromine (or the mixed crystals) would be in equilibrium with a gas-phase which contains much more HBr; from this we deduced that the liquid- and the vapour branches of the t, x-curve for constant pressure (the boiling point line) are much diverged. We tried to prove this by passing gaseous hydrogen bromide through bromine at 0° and analysing both the liquid and the gas. The bromine was placed in a tube furnished at the bottom with a tap by means of which the solution saturated with HBr could be removed. The hydrogen bromide which had bubbled through the bromine was passed through a tube furnished with stopcocks at both ends, from which it finally emerged in a flask over water. After the gas had passed for some time so that it might be taken for granted that the bromine was saturated and the tube completely

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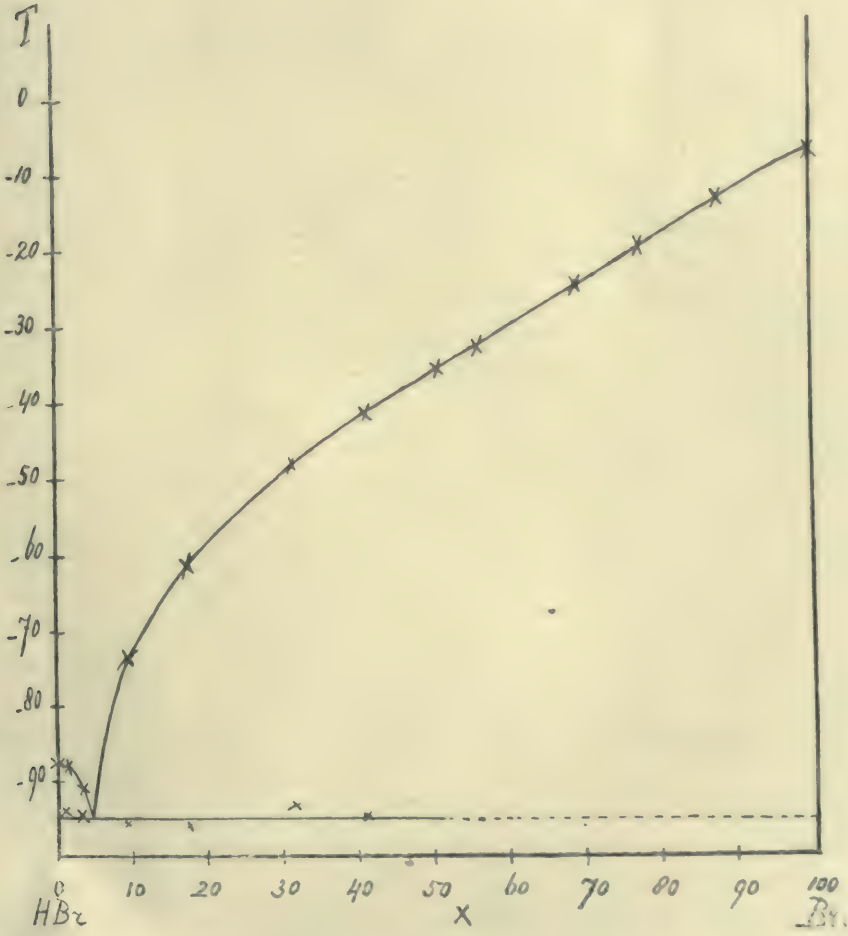
[1]) Only in the case of one tube — 77.6 $^0/_0$ Br_2 — the deviation might amount to about 2 $^0/_0$, at least under a pressure of 5 Atm.; with the others it amounts to at most $^1/_2$ $^0/_0$.



filled with the vapour which was in equilibrium with the liquid the two stopcocks were closed. After introducing aqueous sodium hydroxide by gently opening one of the stopcocks until all HBr and Br had been absorbed, the solution was introduced into a measuring flask and diluted to the mark. An aliquot portion was then titrated at once with KJ and $Na_2S_2O_3$, and in another portion the bromine was all converted into bromide by means of H_2O_2 and then titrated according to VOLHARD with $AgNO_3$ and NH_4CNS. In this way we found the free bromine and the total bromine from which the relation HBr : Br_2 may be calculated. In a similar manner the composition of the liquid was determined. At 0° we found for the liquid 8 mol. °/₀ of HBr and 92 °/₀ of Br_2; for the vapour 87 °/₀ of HBr and 13 °/₀ of Br_2 [1]).

This result renders the existence of a compound in the vapour highly improbable, for if a compound occurs in a binary system in the fluid phases an inward bend is noticed in the p, x- or t, x-curves; the liquid- and the vapour branch approach each other more or less according to the degree of dissociation of the compound. Judging from our observations there can be no question of something of the kind taking place in our case.

We beg to say just a few words as to the significance of these results in connection with the supposition mentioned above. Although we have proved that HBr and Br_2 in a pure state do not form a compound it cannot be denied that facts may be disclosed which plead for the existence of such compounds in solvents. But those facts only relate to solutions which possess electrical conductivity power and in which we must assume a powerful action of the solvent on the dissolved matters: in our case splitting into $H^{\cdot}$- and Br'-ions. One might certainly imagine that the Br'-ion has a tendency to take up Br_2 and to pass into Br'_3-ion without this necessitating the existence of a *compound* HBr_3, but in non-conductive solutions the idea of the existence of compounds HBr_n should, in our opinion, be rejected.

Amsterdam, December 1908. *Inorg. chem. labor. University.*

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[1]) These experiments are being continued.

Botany. — "*Dipsacan and Dipsacotin, a new chromogen and a new colouring-matter of Dipsaceae*". By Miss T. Tammes. (Communicated by Prof. J. W. Moll).

If leaves of *Dipsacus sylvestris* are heated for a few hours in a moist space to a temperature of 60° C., they acquire a fine dark-blue coloration. I have more closely investigated this phenomenon, which once accidentally came to my notice, and have studied the conditions of the formation of the blue colouring-matter *dipsacotin*, its properties and those of the chromogen *dipsacan*, the localisation of the latter and its distribution in the vegetable kingdom. At the same time I have traced the occurrence of *dipsacase*, the enzyme which splits the chromogen.

Here I wish briefly to communicate the chief results of the investigation; a more detailed paper on this subject will be published in Recueil des Trav. bot. Néerl. Vol. V, 1908.

The investigation, which was chiefly carried out with radical leaves of *Dipsacus sylvestris* and *fullonum*, has shown that for the formation of the blue colouring-matter a temperature of at least 35° C. and the presence of water and oxygen are necessary.

Between 35° and 100° C. the rate of formation of dipsacotin increases with the temperature. It is only formed after the death of the leaf. No blue colouring-matter is formed in the living plant, even when exposed for several days to a temperature of 35°—40° C.; the pigment only appears in the dead leaves, when the plant is dying off.

If leaves are dried very rapidly at a temperature above 35° C., no dipsacotin is formed, or only a very small quantity; if, however, during the warming, the leaves are in a moist atmosphere,t hey are coloured blue.

Neither does the blue coloration occur when oxygen is absent. Since it is extremely difficult to free the leaves completely from air, I have proved in another way, that oxygen is necessary. The chromogen can be extracted by warm water, and if the extract is warmed in a space completely shut off from the air, no dipsacotin is formed, even on heating for days together. As soon as the extract is warmed in contact with the air, the blue colour rapidly appears.

The formation of dipsacus-blue is therefore accompanied by an oxidation. Experiments have shown, however, that the colouring-matter does not result directly from dipsacan by oxidation. An intermediate product is first formed, as is shown by the fact that the light yellow extract becomes yellowish red on being heated in a space shut off from the air, and that the yellowish red solution has acquired the property of turning blue even without being heated. In the formation of dipsacotin from dipsacan a chemical transformation, which can only occur on warming, evidently takes place first; the subsequent oxidation can also proceed at the ordinary temperature, although it is greatly accelerated by warming.

Of the properties of dipsacotin I only propose to mention, that this colouring matter is soluble in water, that it is decomposed by sulphuric acid with the formation of a yellowish red product, and that it is decomposed by light; three points in which it differs from indigo.

The chromogen dipsacan is decomposed by acids and by alkalies, and can only exist in a feebly acid solution, such as that of the extract. Acids and alkalies do not, however, even on heating, produce the transformation-product which by oxidation forms dipsacotin. This is formed from dipsacan, not only by warming above 35° C., but also at the ordinary temperature, through the agency of dipsacase, the enzyme occurring in the plant. This perhaps explains an observation made long ago by DE VRIES [1]), that the press-juice of *Dipsacus fullonum* becomes black after a few days' exposure to the air. Probably the juice contains both the chromogen and the enzyme, and the former is decomposed by the latter. That the colour, after oxidation, is black and not blue, may perhaps be attributed to the presence of other substances, or to other chemical reactions taking place simultaneously.

Dipsacan occurs in all organs, even including the flower and the seed, and all tissues, except the pith of the stem, contain it. The cellwall is probably free from dipsacan, as it does not become coloured blue.

The quantity of the chromogen, present in the various organs, depends on internal and external causes. Young parts growing vigorously, contain most. Under favourable conditions of life the quantity is larger than under unfavourable; at temperatures which approach the limits of life of the plant, the quantity of dipsacan is less. Light exercises no direct influence on the presence of the chromogen. In the dark the dipsacan does not disappear from the leaves, but it is formed in new, completely etiolated ones. Dipsacan is therefore not directly related to carbon-assimilation. More probably the chromogen takes part in metabolism, and as it occurs in the plant in such large quantity, and especially in parts growing vigorously, it must indeed be an important substance to the plant. I imagine that dipsacan is continually formed and continually decomposed in the plant, and that the product of transformation, most probably that product which yields dipsacotin on oxidation, is used in various vital processes. In those places, where it is required, it is formed by the enzyme from the dipsacan present, and since it is not oxidized in the living plant to dipsacus-blue, we must conclude, that it is used up at once. Probably therefore dipsacan is the form under which the product used in metabolism, is stored up by the plant. This view not only explains the presence of the enzyme, but also the fact, that no dipsacus-blue is formed during life.

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[1]) HUGO DE VRIES, Een middel tegen het bruin worden van plantendeelen bij het vervaardigen van praeparaten op spiritus. Maandbl. v. Natuurw. 1886, No. 1.

Besides in *Dipsacus sylvestris* and *fullonum*, I have been able to demonstrate dipsacan in several other species of *Dipsacus*, and in various species of the genera *Succisa*, *Scabiosa*, *Knautia*, *Asterocephalus*, *Pterocephalus*, *Trichera* and *Cephalaria*. It is not wanting in any of the members of the order *Dipsaceae* which I have examined, so that I conclude, that it is characteristic of this order. It does not occur in other plants, as was shown by an examination of about 80 species, belonging to widely different orders. Only in the three species of the genus *Scaevola* of the order *Goodeniaceae*, which were at my disposal, I found, after warming parts of the plants in a moist space, that a blue colouring-matter occurs which is doubtless dipsacotin. The occurrence of dipsacan is therefore limited to two closely related natural orders, and a certain systematic value must undoubtedly be attached to it.

Groningen, *Botanical Laboratory*, Nov. 23rd, 1908.

Chemistry. — "*On the bromation of toluol*" and "*On the sulfonisation of benzol sulfonic acid.*" By Prof. A. F. HOLLEMAN and Dr. J. J. POLAK.

(These communications will not be published in this Proceedings).

(January 27, 1909).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday January 30, 1909.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 30 Januari 1909, Dl. XVII).

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Microbiology. — "*The splitting up of ureum in the absence of albumen.*" By Dr. N. L. SÖHNGEN. (Communicated by Prof. S. HOOGEWERFF).

(Communicated in the meeting of October 31, 1908).

§ 1. *General considerations. Ureum as a source of energy.*

Ureum, secreted as a product of the katabolism in the higher organized animal world, leaves the body, dissolved in urine.

As such this nitrogen-compound cannot be assimilated by the higher vegetable world, and hence it would be of no practical importance for us, if there were no fungi, especially certain microbes everywhere in the ground, which changed it into assimilable compounds.

It is for this reason that we have to consider urine, more particularly ureum, as one of the most valuable sources of nitrogen for arable land.

Millions of kilogrammes of the indispensable nitrate-nitrogen are annually in a biological way formed from urine in the ground and are of the greatest use to vegetation.

Nitrogen taken by man and animal as vegetable albumen, leaves the body again for the greater part in the form of ureum, and in this way describes a cycle.

A rough calculation of the quantity of ureum, which in our country is produced by the population and the cattle, gives an idea of the enormous quantity of nitrogen describing this cycle.

The data for the amount of cattle have been taken from *Verslagen en Mededeelingen van de Directie van den Landbouw.* (Reports and Communications of the Board of Agriculture).

The quantity of ureum, daily secreted by the population, amounts to ± 125000 K.G.; by the cattle ± 225000 K.G., making ± 350000 K.G., or ± 350 tons a day.

By biological oxidation, a quantity of nitrate-nitrogen would be produced equal to that found in ± 900 tons of saltpetre.

Annually from the ± 125000 tons of ureum formed, ± 350000 tons of saltpetre could be produced, representing a value of ± 3.5 millions of £. sterling and this, distributed over the 2155000 acres of arable land, would yield ± 160 K.G. of saltpetre pro acre.

That only a trifling part of this enormous mass is utilized for agricultural purposes, need not be proved here. Especially in large towns for hygienic reasons almost all ureum is lost to any useful purpose; on the other hand it would decidedly be of great value for farms in the country, to be more careful about collecting urine.

The above mentioned considerations may serve to draw once more attention to the enormous value represented by ureum as a manure.

In the experiments about microbes decomposing ureum the culture media generally were characterized by the presence of albumen and peptones.

It is true that VON JAKSCH [1]) and BEIJERINCK [2]) have made experiments with salts of organic acids as a source of carbon, but a systematic investigation in this direction has not been made as yet.

VON JAKSCH's investigation in 1881 was especially of importance for the study of the conditions of nutriment of ureum-bacteria. It taught us that carbo-hydrates, salts of fatty acids and of organic multibasic acids can be assimilated.

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[1]) Zeitschrift für Phys. chem. 1881.

[2]) Centralbl. f. Bakt. II, Abt. VII, Bd. 1901.

The so highly interesting studies of BEIJERINCK about the decomposition of ureum by microbes principally treat of the ureum-decomposing organisms which in cultures, on application of his *accumulation-method* in bouillon 10 °/₀ ureum make themselves conspicuous. In the course of the investigation some experiments have been made with culture-liquids, composed of water, 5 °/₀ ureum, 0.025 K_2HPO_4 and 1 °/₀ ammoniumoxalate, natriumacetate, seignette-salt, ammoniumcitrate and ammoniummalate. In these culture-media a strong decomposition of ureum takes place after infection with mould.

The 5 °/₀ ureum added, however, are not entirely decomposed. The easily assimilable compounds, such as ammoniummalate and citrate, give rise to a greater ureum-decomposition, respect. 4°/₀ and 3°/₀, than those which are not so easily assimilated, such as ammoniumoxalate and natriumacetate, in whose presence only 2 °/₀ ureum is decomposed.

The study of the microbes which are found in these cultures, was not continued at that time.

The purpose of this investigation is therefore principally to prove that the life of numbers of ureumbacteria is by no means dependent on the presence of albumen, but that for these ferments the large quantities of carbo-hydrates and salts of organic acids, which for microbial life are available in mould are extremely fit as a source of carbon, whilst at the same time the ureum can serve as a source of energy as well as as a source of nitrogen.

Some preliminary experiments led to the conviction that the most different sources of carbon, in culture-liquids containing these compounds and ureum, dissolved in water, 0,05 °/₀ K_2HPO_4 are excellently fit for the growth of weak as well as for very strong ureum-splitting microbes.

Cultivated in a thin layer of liquid in Erlenmeyer-recipients at ± 33°, being the optimumtemperature of the growth, strong species, especially those producing spores appear; at a low temperature, 15°—23°, less strong splitting ferments, especially micrococci are produced.

The exclusion of other groups and the privilege of the ureum-bacteria in these culture-media is so complete, that the latter mixed with raw materials, such as mould, sewer or ditchmud, after some days contain only ureumsplitting organism.

If one of these cultures, infected with raw material, is put into sterilised liquids of the same composition, the ureum-fermentation also progresses very well there.

Which ureum-splitting species will appear depends upon the composition of the source of carbon added and the degree of alkalinity of the culture-medium.

In § 2 and § 3 we shall revert to this more in detail.

Ureum as a source of energy.

Ureum gives to the ureum-splitters exclusively energy; in no circumstances whatever it is fit to serve at the same time as a source of carbon.

Different experiments which I have made about this, corroborate the truth of former investigations; neither can ureum serve as oxidizable material in the sulphate-reduction; denitrification with ureum is also impossible.

The part that ureum plays in the growth of microbes, is therefore sharply determined. Always the presence of some suitable source of carbon is necessary; this carbon-compound is partly oxidated and therefore also this part serves for energy, partly it is assimilated.

For the above-mentioned oxidation of the source of carbon atmospheric oxygen is used; the quantity necessary is very small, which can be proved by cultivation in bottles with a stopper, which are entirely filled with the culture-liquid.

Only the oxygen dissolved in the culture-liquid is then available for the microbes and nevertheless the ureum-splitting then takes place just as well as when the supply of oxygen is abundant.

If, however, the culture-liquid has previously been made free from oxygen by boiling, after infection no ureum-splitting takes place in a bottle completely filled.

From these experiments follows that a good ureum-splitting is possible, while only very little organic matter is oxidated.

Now it is a fact that on the whole strong splitting ferments show in the cultures a very slight growth and from this it follows that also the quantity of carbon, necessary for the structure of bacterial bodies is very small.

These facts prove that a small quantity of a suitable organic compound, in the presence of ureum, must be sufficient for a complete development of the organisms and a normal ureum-decomposition.

Now, in order to ascertain what part of the sum of energy developed in the culture, is developed in the splitting up of the ureum the minimum quantity of carbon-compound, sufficient for a normal ureum-decomposition and growth, was determined. For this purpose experiments have been made with the afterwards described *Bacillus* *erythrogenes* and *Urobacillus jakschii* in series of culture-liquids, which, besides ureum, contain a diminishing quantity of asparagina or ammoniummalate.

Indeed a very trifling quantity of these materials proves to be sufficient for a normal ureum-decomposition.

From the results of the investigations, laid down in the subjoined table, it follows that the *Bacillus erythrogenes* at a normal growth splits 500 mG. of ureum with 20 mG. of carboncompound whilst the *Urobacillus jakschii* splits 1800 mG. of ureum with 10 mG. of carbon-compound.

With smaller quantities of carbon-compound the growth of both microbes is considerably less than above.

The quantity of energy, which in the *erythrogenes*- and *jakschii*-cultures was developed by the splitting of the ureum, amounts respectively to ± $96^0/_0$ and $99^0/_0$ of the total sum of energy developed in these cultures.

At the same time it appears from these numbers that the less splitting species want a larger quantity of carbon-compound for the decomposition of a certain quantity of ureum than the very strong splitters.

The figures in the subjoined table denote the number of c.c. $N\ H_2SO_4$, necessary for neutralizing 50 c.c. culture-liquid after five days of culture at a temperature of 30°.

The 50 c.c. culture-liquid inocculated with the *Bacillus erythrogenes*, consist of water, in which $0.05\ ^0/_0$ K_2HPO_4 $2\ ^0/_0$ ureum and the carbon-source are dissolved.

The 50 c.c. culture-liquid infected with *Urobacillus jakschii* has, besides $5^0/_0$ ureum instead of $2^0/_0$ ureum, the same composition as the above mentioned.

Decomposition by Bacillus erythrogenes.

Quantity of carbon-source in milligrammes	50	40	30	20	10	5
Decomposition if the latter is asparagine	18.5	17.5	17	17	13	8
Decomposition if the la'ter is amm. malate	19.8	17.9	18.5	18.0	14.2	9.5

Decomposition by Urobacillus jakschii.

Decomposition if the latter is asparagine	61.5	60	59	60	54	42
Decomposition if the latter is amm. malate	60	58	60	59	56.5	39

§ 2. *Calciumsalts of organic acids as a carbonsource for ureum-splitting microbes.*

The organic acids proceeding from plants or produced by fermentation thereof are principally neutralized in arable soil by the frequently occurring calciumcarbonate.

The general occurrence, therefore, of these salts in the soil caused, for the following investigations, calcium-compounds of organic acids to be chosen in the first place as a source of carbon for ureum-splitting bacteria.

If in a culture-liquid, containing these salts and ureum, dissolved in water to which 0.05 K_2HPO_4 is added, ureum is split, the ammonium-carbonate formed will not directly bring about a considerable increase of alkalinity of the medium, but in the first place it will be neutralized by the calciumsalt and that according to the formula:

$$\mathrm{Ca\,R} + (\mathrm{NH_4})_2\,\mathrm{CO_3} = \mathrm{Ca\,CO_3} + (\mathrm{NH_4})_2\,\mathrm{R}$$

Therefore the calcium-compounds of the organic acids exercise a retarding influence on the alkalinity; for not until all the calcium is united with the carbonic acid formed, the alkalinity will advance rapidly; then the culture-liquid is like one that contains an ammoniumsalt of an organic acid as source of carbon. This is treated of in § 3.

But it is especially because of the existence of this period of rest before the increase of alkalinity, that cultures with calciumsalts of organic acids are so particularly fit for the accumulation of less strong splitting organisms, by which means every opportunity is afforded for study of these kinds, which are otherwise so rapidly supplanted.

The cause that during this first period also the ureum-splitters have the advantage of all the microbes contained in the raw infection-material, so that the latter are already then entirely supplanted is that their specific source of energy, the ureum, is at their disposal.

So if we want to get an insight into the numerous kinds of weak ureum-splitters, we have to make a plate-culture before all calcium is united with carbonic acid.

As a rule a good result is obtained when after 2 or 3 days the plate-making takes place on meat-gelatine or on a culture-medium, composed of water, 10°/₀ gelatine, 0.05°/₀ K_2HPO_4, 0.05 NH_4Cl and 0.5 °/₀ calc. malate.

These experiments give a fair idea of the great number of ureum-splitting microbes which the soil contains; they follow each other as the process proceeds and as the alkalinity increases, till at last the strongest, the most powerful hydrolysing kinds are left.

To give a detailed description of the many weak ureum-splitting kinds that exist, would be of hardly any use.

During my experiments in October, November, and December 1904 in the *Microbiological Laboratory*, under the guidance of Prof.

BEIJERINCK at Delft, there regularly occurred in these cultures a microbe which drew the attention by the formation of a red and yellow colouring-matter on meat-agar and meat-gelatine. The colonies are of a bright yellow colour, whilst a red colouring-matter diffuses in the culture-plate.

This bacterium shows itself more especially in cultures with citrate and tartrate in large numbers, so that in using these salts the above mentioned species can be obtained in great numbers.

If in the same culture-liquid inocculation is repeated twice or three times at a temperature of 23° and a titre of ± 35 c.c. N. per 100 c.c. culture-liquid, this bacterium is often accumulated almost to pure culture.

Description of Bacillus erythrogenes.

Bacillus erythrogenes are among the very strong oxidating ferments; both sugars and salts of organic acids and also albumen are assimilated. In tap water 0.05 % $K_2 HPO_4$ a fair growth takes place in the presence of ureum, if one of the following compounds as a carbon-source is added: glucose, maltose, cane-sugar, asparagine, calcium- and natriumsalts of the volatile fatty acids (except of formic acid, which gives a slight growth) and the multibasic acids, such as apple acid, lactic acid, lemon acid, argol acid and amber acid (except oxalic acid).

Milk appeared to be a very suitable culture-medium. The development herein is attended by the appearance of a disagreeable sweet smell.

Even calciumhumate added as a carbon-source causes growth and therefore ureum-splitting.

Amylum, however, is not affected, so that evidently no diastatic enzym is formed.

The yellow colouring-matter belongs to the body of the bacteria and arises independent of the composition of the medium; however for its formation the influence of light is necessary.

The red, diffusing colouring-matter arises only in case the feeding takes place with albumen and the light is excluded. Arisen in the dark, this colouring matter will soon be decomposed when exposed to the light.

Cultivated on meat-agar while light is excluded, the white colony shows itself on a fine red diffusion-field; cultivated in the presence of light, there arises a bright yellow colony on a colourless field.

What influence the two colouring matters have on the vitalfunctions of the microbe, could not be stated.

Gelatine is melted by the strong splitting varieties, not by the weak ones.

The length of the bacterium amounts to 2—4 μ
Breadth 1—1.5 μ

The bacterium is endowed with the power of motion, and in liquids mostly occurs as a double bar; on solid media it sometimes forms strings.

No formation of spores takes place.

The optimum of the growth lies near ± 30°.

The optimum of its urease near ± 51°.

Ureum-splitting by the strongest species is found in the subjoined table.

The figures denote the number of c.c. $^1/_{10}$ N. H_2SO_4, which are necessary for the neutralization of 10 c.c. culture-liquid.

The culture has taken place at 43°.

In bouillon with ureum.

After days	1	2	3	4.
$2^0/_0$ ureum	13.5	33.	45	44.
$6^0/_0$ ureum	19.	45	68	68.

If we compare the species described here with those isolated by Löhnis [1]), they prove to agree in size and formation of a double colouring-matter; striking is the difference in the power of splitting ureum.

In his experiments a *bacillus erythrogenes* split in bouillon $2^0/_0$ and $5^0/_0$ ureum resp. $^1/_{10}\ ^0/_0$ and $1^0/_0$ ureum, whilst the one described here splits in bouillon $2^0/_0$ and $6^0/_0$ ureum resp. $1^1/_3\ ^0/_0$ and $2^0/_0$.

The less strong species, isolated here, still split in the culture-liquids named $^1/_2\ ^0/_0$ and $1\ ^0/_0$ ureum respectively.

So it is clear that the species *Bacillus erythrogenes* includes varieties of very different ureum-splitting power.

The powerful splitters are at the same time characterized by the possession of tryptic enzymes.

§ 3. *Ammoniumsalts of organic acids as a carbon-source for ureum-splitting microbes.*

Ammoniumsalts of organic acids are in media, which at the same time contain ureum and anorganic salts, superior to any other compounds for the development of strong ureum-spliting microbes.

Both the split ureum and the ammoniumcarbonate of the oxidated ammoniumsalt that has become free contribute to the rapid rise of the alkalinity of the culture-liquid.

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[1]) Centr bl. f. Bakt. Abt. XIV Bd 1905.

Provisional experiments proved that with a ureum-quantity of ± 5 % in these cultures the best results could be obtained; with this ureum concentration growth is still very good.

In a way quite analogical with the ammoniumsalts behave different sugars as carbon-sources for ureumsplitters; the species which are most remarkable generally agree with the powerful species isolated by MIQUEL.

A culture-liquid consisting of:

100 water

0.05 K_2HPO_4

1 ammoniummalate

5 ureum

infected with ± two gr. of mould or sewage and cultivated at ± 33° contains after 48 hours, sometimes even after 36 hours only ureum-splitting ferments. A total supplanting of all other organisms has taken place in that short time.

The decomposition of the ureum takes place in presence of easily assimilated carbonsources, such as malate and lactate, more rapidly than with compounds which are not so easily assimilated such as tartrate or acetate.

Malate is also for these organisms an exceedingly easily assimilable compound, as is generally the case; lactate, citrate, succinate, tartrate, butyrate and acetate follow next.

When, however, in a culture with one of these salts the final titre has been reached, the same powerful species are on the whole observed in malate as well as in tartrate and acetate cultures.

Now if we examine the sorts succeeding each other in these culture-liquids, it appears that, when sown upon meat-gelatine $^1/_2$ % ureum or ammoniummalate-gelatine $^1/_2$ % ureum, already after two days, when the titre is ± 60 c.c. N. per 100 c.c. culture-liquid, the number of micrococcis and melting bacteria rapidly diminishes; whilst the alkalinity increases, bacteria forming spores together with a ureum-splitter not forming spores take their place.

The many weak splitting organisms observed in the cultures with calciumsalts rapidly die off.

After 3 or 4 days only very strong hydrolysing microbes are left, whilst micrococcis and melting species have disappeared.

The growth on neutral meat-gelatine of the species found in strongly alkaline liquids is very slight or does not succeed at all.

In general the colonies on meat-gelatine 1 % ureum or ammonium malate-gelatine 1 % ureum are characterized by their small dimensions, whilst a field of calciumphosphate- and calciumcarbonate-crystals surrounds them.

After 5 or 6 days the titre has risen to a maximum of ± 125 c.c. N. per 100 c.c. of culture-liquid, so that ± 4% ureum has been split.

The 4 or 5 species present are the *Urobacillus leubiï* (Beijerinck) and the most powerful species described by Miquel, the *Urobacillus maddoxiï, freudenreichiï* and *duclauxiï* together with a species not yet described and not forming spores, which will be called *urobacillus jakschiï.*

After infection of cultures with ammoniummalate it is especially the *Urobacillus maddoxii* and *urobacillus duclauxii* together with the *Urobacillus jakschii* which predominate. Sometimes the *Urobacillus jakschii* supplants the two other species almost entirely and is almost accumulated to pure cultivation.

If we start from pasteurized material, it is especially the *Urobacillus maddoxii* and *Urobacillus duclauxii* which make themselves conspicuous.

In these culture-liquid the *Urobacillus pasteurii* Beijerinck did not occur, so that the latter may be said to belong to the ureum-bacteria which positively want albumen for their growth.

For the description of the *Urobacillus leubii, freudenreichii, maddoxii* and *duclauxii* it is sufficient to mention the chief characteristics.

The *Urobacellus jakschii,* however, will be described more in details.

Urobacillus leubii (Beijerink).

Urobacillus leubii, which generally occurs in the *Vorflora* of Beijerinck's accumulation-experiments, is a little moving bar which can get oblong spores.

On meat-gelatine with ammoniumcarbonate it is difficult to distinguish this species from *urobacillus pasteurii.* Inocculated from this medium on neutral meat-gelatine it grows into two species of colonies: viz. into yellow, troubled, thin colonies forming spores and into glassy, transparent colonies free from spores.

The growth is, however, upon meat-gelatine with ammoniumcarbonate much better than upon neutral meat-gelatine.

The spores can bear boiling heat and can be dried.

Gelatine is not melted.

In bouillon 6 % ureum 2½ % ureum is split in 4—5 days

Urobacillus freudenreichii MIQUEL,

Urobacillus freudenreichii is a little moving bar, 5—6 μ in length, 1 μ broad; on a firm medium it grows into long threads.

Elliptic glittering endospores are formed, which can stand a heat of 94° for two hours.

Neutral gelatine is slowly melted by the irregularly formed colonies, whilst gelatine to which ureum has been added, is not melted and the colonies on it assume the characteristic globular form.

2 °/₀ ureum in bouillon are decomposed within 4 days at 30°—35°.

MIQUEL isolated this species out of air, riverwater, soil and from the excrements of ruminants.

Urobacillus maddoxii MIQUEL.

A little moving bar, 3—6 μ long, 1 μ broad, forming oval endospores, which are able to bear a heat of 94° for two hours.

On neutral meat-gelatine it does often not develop, on ammoniacal gelatine the growth is rather good.

Within 3 days 2 °/₀ ureum in bouillon is split.

The bacterium has been isolated from sewage and river-water.

Urobacillus duclauxii MIQUEL.

Like the two preceding species moving; length 2—10 μ, breadth 0,6—0,8 μ.

The bacterium forms small elliptic endospores which are able to bear a heat of 95° for 2 hours.

In a neutral medium no growth arises, on ammoniacal meat-gelatine or on meat-gelatine provided with ureum there arise very small hardly observable colonies which are surrounded by crystals.

The gelatine does not melt, but it becomes like viscous after 40 –50 days.

2°/₀ ureum in bouillon are decomposed within 24 hours.

Urobacillus jakschii.

Urobacillus jakschii is a small quickly moving bar in a culture-medium that is not too alkaline; if some percents of the ureum in it have been split, the motion stops.

Length of the bacterium 5—7 μ; breadth 1—1.5 μ. Spores are not formed.

On neutral meat-gelatine growth is seldom obtained; if, however ammoniumcarbonate or 1 $^{0}/_{0}$ to 2 $^{0}/_{0}$ ureum is added, there arise small coli-like colonies, surrounded by a wreath of calciumphosphate crystals.

The gelatine is not melted, but after a month, it is viscous.

2 $^{0}/_{0}$ ureum in bouillon are split in 24 hours. Of 10 $^{0}/_{0}$ ureum in bouillon 6—7 $^{0}/_{0}$ are changed into ammoniumcarbonate.

In culture-media containing the necessary anorganic salts together with ureum, a good growth is obtained with the following compounds after infection: pepton, asparagine, glucose, cane-sugar, maltose, citrates, lactates, tartrates, and salts of volatile fatty acids (except salts of formic acid).

§ 4. *Irisating cultureplates.*

The faculty in bacteria of splitting ureum can according to the method of Beijerinck by means of the yeast-water-gelatineplate 2 or 3 $^{0}/_{3}$ ureum, be proved in a very elegant way by the *Iris-phenomenon* formed on this culture-medium by those bacteria.

It is supposed that the ammoniumcarbonate getting free at the decomposition of ureum causes the phenomenon, in consequence of the precipitation of calciumcarbonate and -phosphate.

An explication of the origin of the irisphenomenon on the yeast-water ureum-gelatineplate, has, however, its difficulties, the culture-plate being so complicated that it is not easy to get an exact idea of the process.

In the experiments with ureumbacteria on plates composed of water, 0.5 $^{0}/_{0}$ calcium salt of an organic acid, 1 $^{0}/_{0}$ ureum, 0.05 $^{0}/_{0}$ K_2HPO_4, 10 $^{0}/_{0}$ gelatine or 1.5 $^{0}/_{0}$ agar, the iris-phenomenon often produced itself.

The possibility of composing a simple culture-plate, if possible coagulated by agar, which produces the iris-phenomenon in a beautiful way, seemed not to be excluded, when the above facts were taken into consideration.

In this way corresponding phenomena on the yeast-water-ureum-gelatineplate and the irisating of more complicated culture-plates might be generally explained.

After some trials I succeeded in the following manner in composing a plate which entirely answers the requirements.

In pure water agar ± 0,5$^{0}/_{0}$ calciummalate or -lactate and 0,05 $^{0}/_{0}$ ammoniumcitrate are dissolved; the melted agar is cooled down to the still just liquid state, after which a K_2HPO_4 solution is added, till a slight opalizing is observed: now the culture-plate is formed of this material.

This culture-plate is, if made with care, almost clear. The calciumphosphate that has been formed remains dissolved with the ammoniumcitrate. A drop of ammoniumcarbonatesolution on this medium causes the irisphenomenon, while after some moments produces itself a precipitate round the drop.

This phenomenon shows itself in quite the same way, if, instead of agar, gelatine is taken.

The irisating field and the precipitate are microscopically and chemically identical to those which are produced on the yeast-water-ureum-gelatineplate.

If the culture-medium contains no phosphate, ammoniumcarbonate put on it gives a very slight field of $CaCO_3$; a drop of ammonia produces no irisating field at all.

If, however, only calciumphosphate, dissolved in ammoniumcitrate, is present as the only calciumcompound, ammoniumcarbonate and also ammonia on such a plate cause an extremely fine irisating field.

If ± 2°/₀ ureum is added to this plate ureum-splitting microbes cause thereon the "*irisphenomenon*".

From these experiments it appears that the calciumphosphate-precipitation has to be considered as the real cause of the irisating of the culture-medium, whilst the calcium-carbonate formed at the same time plays a subordinate part.

Accordingly the irisating of culture-plates by certain bacteria growing on them and the *irisphenomenon* of BEIJERINCK have to be regarded as a consequence of the precipitation of calciumphosphate in the first and of calciumcarbonate in the second place.

§ 6. *Results obtained.*

1. Decomposition of ureum, in the absence of albumen, may take place by different microbes, if some suitable carbon-source is present.

2. In cultures in which ureum-splitting takes place, ± 98°/₀ of the total energy is developed by the decomposition of the ureum.

3. Cultures with calciumsalts of organic acids as a carbon-source, are extremely fit for getting weak splitting ureumbacteria. The *bacillus erythrogenes* occurring herein has been described more in detail.

4. Cultures with ammoniumsalts of organic acids or sugars as

a carbon-source, rapidly lead to the accumulation of strong ureum-splitting bacteria forming spores and the *urobacillus jakschii* forming no spores.

5. The irisating of culture-plates and the "irisphenomenon" on the yeast-water-gelatineplate are the consequence of the precipitation of calciumphosphate, whilst calciumcarbonate formed at the same time plays a subordinate part in it.

At the end of this investigation I beg to express my sincere thanks to Professor M. W. Beijerinck for advising and supporting me in these experiments wherever and whenever he could.

Physics. — "*Statistical Theory of Capillarity.*" By Dr. L. S. Ornstein. (Communicated by Prof. H. A. Lorentz).

(Communicated in the meeting of December 24 1908).

In a paper [1] published in 1893 van der Waals has developed a theory of capillarity, which leads to results agreeing sufficiently with observation, as has been shown by the experiments of Dr. E. O. de Vries.

The methods used in the above mentioned paper have been reproduced with only a slight change in the lectures of van der Waals recently published by Prof. Ph. Kohnstamm.

Both in the paper and in the treatise the hypothesis [2] is introduced, that the entropy of an element of volume is a function only of the number of molecules it contains and of that of their collisions.

By the statistical method of Gibbs we can deduce the condition of equilibrium for the capillary layer without using a hypothesis of this kind and we can easily show that it must be true when certain conditions are fulfilled. This is the object of the present paper in which I shall also determine some quantities that play a part in the theory of capillary action.

§ 1. Let us suppose that n spherical molecules of diameter σ, perfectly rigid and elastic, are enclosed in a vertical cylinder of height Z, and of unit of horizontal section, closed at the top and the bottom by horizontal walls. Let the axis of z be drawn upward and let us further suppose that the molecules exert attractive forces on each other up to distances which are large in comparison with the diameter σ and with the distance of neighbouring molecules. I shall denote by $-\varphi(f)$ the potential energy of this attraction for a pair of molecules whose centres are at a distance f and I shall suppose that $\varphi(f)=0$ for values of f which are large compared with σ (and the distance between neighbouring molecules) but small compared with finite lengths, the same being also true of the function $\psi(f)$ determined by the equation

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[1] J. D. v. d. Waals, Thermodynamische theorie der capillariteit in de onderstelling van continue dichtheidsverandering. Verh. d. K. A. v. W. Deel I. 8. 1893.

[2] Compare l. c, p. 16.

$$f\varphi(f)\,df=-d\psi(f)\quad .\ .\ .\ .\ .\ .\ .\ .\ (1)$$

Let us now consider a canonical ensemble with modulus θ built up of N systems of the above kind.

We divide the volume of the cylinder by horizontal planes into a great number k of elements of a height $dz_\varkappa$ this height being large compared with σ and small compared with the distance at which the molecules sensibly attract each other. I shall further suppose that the potential energy of attraction changes but little over a distance of the order of magnitude $dz_\varkappa$ [1]).

We shall determine the number, or, let us say, the "frequency" ζ of those systems in the ensemble in which there are $n_1 \ldots n_\varkappa \ldots n_k$ molecules respectively in the elements $dz_1 \ldots dz_\varkappa \ldots dz_k$. I shall suppose that the numbers $n_\varkappa$ are very large; their sum being n we have the relation

$$\sum_1^k n_\varkappa = n.\quad .\ .\ .\ .\ .\ .\ .\ (I)$$

The number of molecules per unit of volume in the element $dz_\varkappa$ (the molecular density) will be represented by $\mathrm{n}_\varkappa$.

I shall consider the mutual energy of a pair of molecules as belonging for one half to the first and for the other half to the second of the molecules. The energy determined in this way is the same for all the particles of the layer $dz_\varkappa$. I shall represent this energy per molecule by $\varepsilon_\varkappa$.

The total potential energy can therefore be represented by

$$\sum_1^k n_\varkappa \varepsilon_\varkappa.$$

The frequency [2]) in question is given by the formula

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[1]) For the sake of simplicity I shall take the elements $dz_\varkappa$ of equal magnitude; our result will be that $\frac{n_\varkappa}{dz_\varkappa}=\mathrm{n}_\varkappa$ (the molecular density) is a function of $z_\varkappa$ showing that we do not lose in generality by this simplification.

[2]) In explanation of the formula (II) the following may be observed. Let us consider a system constituted of n molecules of the kind above described enclosed.

$$\zeta = N (2\pi m\Theta)^{\frac{3}{2}n} e^{\frac{\Psi}{\Theta}} n! \prod_{1}^{k} \frac{1}{n_{\varkappa}!} (\omega_{\varkappa}\, dz_{\varkappa})^{n_{\varkappa}} e^{-\frac{n_{\varkappa}\varepsilon_{\varkappa}}{\Theta}} \quad . \quad . \quad . \quad (II)$$

§ 2. The properties of an observed system are identical with those

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in a vessel of the volume V. And let us imagine a canonical ensemble built up of N systems.

In this ensemble the number of systems — having the coordinates of the centres of the molecules between x_1 and $x_1 + dx_1 \dots z_n$ and $z_n + dz_n$ and the components of the velocities of these points between $\dot{x}_1$ and $\dot{x}_1$ and $\dot{x}_1 + dx_1 \dots$ $\dot{z}_n$ and $\dot{z}_n + d\dot{z}_n$ — amounts to

$$N m^{3n} e^{\frac{\Psi - \varepsilon}{\Theta}} d\dot{x}_1 \dots d\dot{z}_n\, dx_1 \dots dz_n, \quad . \quad . \quad . \quad . \quad . \quad (a)$$

Here, the energy of the system is expressed by ε, and Ψ is a constant for the ensemble depending on Θ and V. The value of Ψ can be found by integrating (a) with respect to the coordinates and the velocities. The result of this integration must be N, which yields a relation for Ψ. The number of the systems in which the velocities have any values, but whose coordinates are lying between the specified limits is obtained by integrating (a) over the velocity components from $-\infty$ to $+\infty$.

The energy ε is given by the relation $\varepsilon = \varepsilon_q + \sum_{1}^{n} \frac{1}{2} m (\dot{x}^2_\nu + \dot{y}^2_\nu + \dot{z}^2_\nu)$ in which ε_q is the total potential energy and m the mass of a molecule. Therefore the result of the integration is

$$N (2\pi\Theta m)^{\frac{3}{2}n} e^{\frac{\Psi - \varepsilon_q}{\Theta}} dx_1 \dots dz_n \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

Let us now divide the volume V into k elements $dV_1 \dots dV_\varkappa \dots dV_k$. If $n_\varkappa$ molecules are situated in an element of volume $dV_\varkappa$ the $3n_\varkappa$ coordinates of their centres may still vary between certain limits; in other terms, a certain extension is left open to the point representing these coordinates in a $3n_\varkappa$-dimensional space. I shall represent the magnitude of this extension by

$$\chi\, (n_\varkappa, dV_\varkappa).$$

The repulsive forces between the molecules are accounted for by excluding from the $3n_\varkappa$-dimensional space $(dV_\varkappa)^{3n_\varkappa}$ all those parts in which there exists a relation of the form

$$(x_\nu - x_\mu)^2 + (y_\nu - y_\mu)^2 + (z_\nu - z_\mu)^2 < \sigma^2 \quad . \quad . \quad . \quad . \quad (c)$$

between the ordinary coordinates of the centres of two molecules. We can represent $\chi\, (n_\varkappa, dV_\varkappa)$ by

$$\int dx_1 \dots dz_{n_\varkappa} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (d)$$

where the integration has to be extended over the whole space $(dV_\varkappa)^{3n_\varkappa}$ with the exception of the parts determined by (c). By a simple reasoning we can show of the system of maximum frequency in an ensemble (whose modulus

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that with a fair approximation $\chi(n_\varkappa, dV_\varkappa)$ can be represented by

$$(\omega_\varkappa \, dV_\varkappa)^{n_\varkappa} \quad . \; . \; . \; . \; , \; . \; . \; . \quad (e)$$

where $\omega_\varkappa$ is a function of $n_\varkappa$. I have calculated for ω the approximate value.

$$log\, \omega = - n\left(\frac{2}{3}\pi\sigma^3\right) - \frac{5}{16} n^2 \left(\frac{2}{3}\pi\sigma^3\right)^2$$

(Cf my dissertation and also these Proceedings 1908 p. 116).

The extension of the $3n$ dimensional space covered by the systems containing $n_1 \, . \, . \, n_\varkappa \, . \, . \, n_k$ definite molecules in the elements $dV_1 \, . \, . \, dV_\varkappa \, . \, . \, dV_k$ can now be represented by

$$\prod_1^k \chi(n_\varkappa, dV_\varkappa).$$

The extension covered by all possible systems of this kind amounts to

$$n! \prod_1^k \frac{\chi(n_\varkappa, dV_\varkappa)}{n_\varkappa!} .$$

In the potential energy we may neglect the repulsive forces, these forces having been already taken into account by the exclusions (c). Supposing that the energy is the same for all the molecules of an element $dV_\varkappa$ we can represent the total potential energy by the formula

$$\sum_1^k n_\varkappa \varepsilon_\varkappa ,$$

For the frequency we find

$$\zeta = N(2\pi\Theta m)^{\frac{3}{2}n} e^{\frac{\Psi}{\Theta}} n! \prod_1^k \frac{\chi(n_\varkappa, dV_\varkappa)}{n_\varkappa!} e^{-\frac{n_\varkappa \varepsilon_\varkappa}{\Theta}} ,$$

or, introducing the function ω by means of (e)

$$\zeta = N(2\pi\Theta m)^{\frac{3}{2}n} e^{\frac{\Psi}{\Theta}} n! \prod_1^k \frac{(\omega_\varkappa dV_\varkappa)^{n_\varkappa}}{n_\varkappa!} e^{-\frac{n_\varkappa \varepsilon_\varkappa}{\Theta}}$$

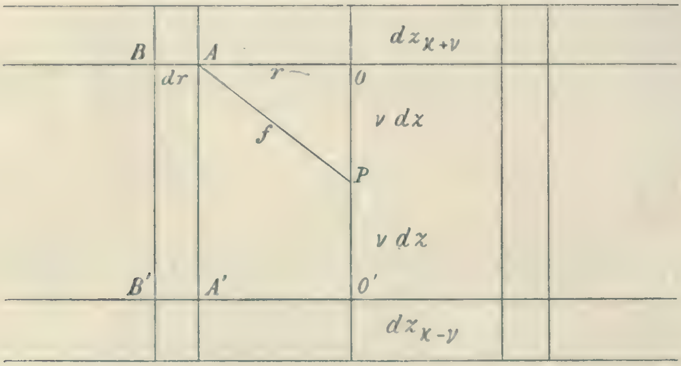
The formula (II) is a direct consequence of the last equation.

As we are treating a case in which there are differences in density in the system of maximum frequency, the question arises as to whether these differences have any influence on the value of the function ω. If it were so, this function would depend not only on n, but also on the derivatives of this quantity with respect to z.

The difference in question really has an influence on the *energy*, but in consequence of the hypothesis of p.p. 526 and 527 the density changes so little along the length $dz_\varkappa$ and the value of the exclusions at the limits of $dz_\varkappa$ is so small in comparison with the value of those originating from the molecules of $dz_\varkappa$ itself, that we may consider $\omega_\varkappa$ as depending only on $n_\varkappa$. This, however, will be true no longer if the sphere of action of the attractive forces is not large in comparison with σ; for this case the following theory would have to be modified considerably.

is proportional to the absolute temperature of the system).[1]

In order to find the condition of equilibrium we have only to determine the values of the numbers n_κ that make the quantity ζ or $\log \zeta$ a maximum. Before we proceed to this investigation we have to express the quantity ε_κ in the numbers n_κ.



Let us suppose that P is a point of the layer dz_κ. We shall try to determine the potential energy for a molecule situated at that point. Consider first the contributions from the molecules situated in two plane layers at a distance νdz from P. We shall indicate these layers by $dz_{\kappa-\nu}$ and $dz_{\kappa+\nu}$. We cut from these layers cylindrical rings by circular cylinders having OPO' as axis and as basis circles with

$$OA = O'A' = r \text{ and } OB = O'B' = r + dr$$

as radii.

The number of the molecules in these elements amounts to

$$2\,\pi\, r dr\, dz\, (n_{\kappa-\nu} + n_{\kappa+\nu}).$$

Considering as equal the distance of all these molecules from P and representing it by f, we find for their contribution to the potential energy of P

$$-\,\pi\, r dr\, dz\, (n_{\kappa-\nu} + n_{\kappa+\nu})\, \varphi(f) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now we have

$$r^2 + (\nu dz)^2 = f^2$$

and therefore

$$r dr = f df \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Taking into account (1) and (3) we can replace (2) by

$$\pi dz\, (n_{\kappa-\nu} + n_{\kappa+\nu})\, d\psi(f) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

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[1] Cf my dissertation § 4 p. 15.

The total contribution to $\varepsilon_\varkappa$ from all the molecules of the layers $dz_{\varkappa-\nu}$ and $dz_{\varkappa+\nu}$ is found by integrating (4) with respect to f from νdz to ∞. Proceeding in this way we find

$$-\pi dz\,(\mathfrak{n}_{\varkappa-\nu}+\mathfrak{n}_{\varkappa+\nu})\;\psi(\nu dz)\quad \ldots\ldots \quad (5),$$

from which formula the energy per molecule in the layer $dz_\varkappa$ can be calculated by adding up all the values of this expression which are such that $\psi\,(\nu dz)$ differs from 0.

In this way we find

$$\varepsilon_\varkappa=-\pi dz\sum_\nu(\mathfrak{n}_{\varkappa-\nu}+\mathfrak{n}_{\varkappa+\nu})\;\psi(\nu dz)\quad \ldots\ldots \quad (5')$$

For the potential energy of the system we have the formula

$$\sum_1^k n_\varkappa\varepsilon_\varkappa=-\pi\,dz\sum_1^k n_\varkappa\sum_\nu(\mathfrak{n}_{\varkappa-\nu}+\mathfrak{n}_{\varkappa+\nu})\;\psi(\nu dz)\quad . \quad (III)$$

§ 3. We may now proceed to the determination of the condition for the maximum. Consider therefore the change of log ζ when we give the variation $\delta n_\varkappa$ to the numbers $n_\varkappa$. These variations are subjected to the equation

$$\sum_1^k\delta n_\varkappa=0\quad \ldots\ldots\ldots\ldots \quad (IV)$$

In the following investigation we may replace $n_\varkappa!$ by $n_\varkappa^{n_\varkappa}e^{-n_\varkappa}$. We find for $\delta\log\zeta$

$$\delta\log\zeta=\sum_1^k\left[-\log\mathfrak{n}_\varkappa-1+\log\omega+\mathfrak{n}_\varkappa\frac{d\log\omega_\varkappa}{d\,\mathfrak{n}_\varkappa}\right]\delta n_\varkappa+$$

$$+\frac{\pi dz}{\Theta}\left\{\sum_1^k\delta n_\varkappa\sum_\nu\psi(\nu\,d\,z)\,(\mathfrak{n}_{\varkappa-\nu}+\mathfrak{n}_{\varkappa+\nu})+\right.$$

$$\left.+\sum_1^k n_\varkappa\sum_\nu\psi(\nu\,d\,z)\,(\delta\,\mathfrak{n}_{\varkappa-\nu}+\delta\,\mathfrak{n}_{\varkappa+\nu})\right\}\quad . \; . \quad (V)$$

It is easily seen that the two sums, with which $\frac{\pi dz}{\Theta}$ is multiplied are equal, both consisting of the same terms, and further that each of them is equal to

$$-\frac{1}{\pi dz}\sum_1^k\varepsilon_\varkappa\,\delta\mathfrak{n}_\varkappa.$$

Attending to the condition (IV) in the usual way, we find that the numbers $n_\varkappa$ in the system of maximal frequency must fulfil the condition

$$log \frac{\omega_\varkappa}{n} + n_\varkappa \frac{d \, log \, \omega_\varkappa}{dn_\varkappa} - \frac{2\varepsilon}{\Theta} = \mu , \ldots \ldots \quad (VI)$$

whereas the second variation of $log \, \zeta$, $\delta^2 \, log \, \zeta$ given by the formula

$$\delta^2 \, log \, \zeta = \sum_1^k \frac{\delta n_\varkappa^2}{2n_\varkappa} \left(-1 + \frac{d}{dn_\varkappa} \left(n_\varkappa^2 \frac{d \, log \, \omega_\varkappa}{dn_\varkappa} \right) \right) +$$

$$+ \frac{\pi dz}{\Theta} \sum_1^k \delta n_\varkappa \sum_\nu \psi (\nu \, d \, z) (\delta \, n_{\varkappa-\nu} + \delta n_{\varkappa+\nu}) \quad , \quad . \quad (VII)$$

must be essentially negative.

The first conditions are equivalent to those given by VAN DER WAALS. It is easy to give the equation (VI) the form which is assigned to it by VAN DER WAALS. We have only to introduce the hypothesis that n changes continually with the height and then to calculate the energy $\varepsilon_\varkappa$.

We obtain in this way [1]

$$log \frac{\omega_\varkappa}{n_\varkappa} + n_\varkappa \frac{d \, log \, \omega_\varkappa}{d \, n_\varkappa} + \frac{2a \, n_\varkappa}{\Theta} + \frac{1}{\Theta} \sum_1^\infty C_{2s} \frac{d^{2s} n_\varkappa}{d \, z_\varkappa^{2s}} = \mu . \text{ }^2) \quad . \quad (VI')$$

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[1] To calculate $\varepsilon_\varkappa$ we proceed as follows. On account of our hypothesis we can write

$$n_{\varkappa-\nu} + n_{\varkappa+\nu} = 2n_\varkappa + 2 \frac{(\nu dz)^2}{2!} \frac{d^2 \, n_\varkappa}{d \, z_\varkappa^2} + \ldots 2 \frac{(\nu dz)^{2s}}{(2s)!} \frac{d^{2s} n_\varkappa}{dz_\varkappa^{2s}} \ldots$$

Introducing this into the formula for $\varepsilon_\varkappa$ and putting

$$2\pi \int_0^\infty \psi (z) \, dz = a ,$$

$$\frac{2\pi}{(2s)!} \int_0^\infty z^{2s} \, \psi (z) \, dz = \frac{1}{2} C_{2s} ,$$

we find for $\varepsilon_\varkappa$

$$\varepsilon_\varkappa = - a \, n_\varkappa - \frac{1}{2} \sum_1^\infty C_{2s} \frac{d^{2s} n_\varkappa}{dz_\varkappa^{2s}} , \ldots \ldots \quad (6)$$

I shall write for $\varepsilon_\varkappa$ also

$$\varepsilon_\varkappa = - a \, n_\varkappa + \varepsilon_{c\varkappa} . \ldots \ldots \quad (6')$$

It is only in the capillary layer that the quantity $\varepsilon_{c\varkappa}$ differs from zero.

[2] We may mention as another advantage in the above deduction of (VI′) that

§ 4. Before I proceed to the discussion of the stability I shall consider the equation (VI). Using (6′) we can put for it

$$log \frac{\omega_x}{n_x} + n_x \frac{d \log \omega_x}{d n_x} + \frac{2an_x}{\Theta} - \frac{2\varepsilon_{cx}}{\Theta} = \mu \dots \quad . \quad . \quad . \quad . \quad (VI'')$$

Subtracting the equation (VI″) taken for the height $z_x + dz_x$ from the corresponding one relating to the height z_x we obtain

$$\left(-\frac{1}{n_x} + 2 \frac{d \log \omega_x}{dn_x} + n_x \frac{d^2 \log \omega_x}{dn_x{}^2} + \frac{2a}{\Theta} \right) \frac{dn_x}{dz_x} = \frac{2}{\Theta} \frac{d\varepsilon_{cx}}{dz_x} . \quad . \quad (7)$$

If we introduce the function p, determined by the equation

$$\frac{p}{\Theta} = n - n^2 \frac{d \log \omega}{dn} - \frac{an^2}{\Theta} , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

— which quantity represents the pressure in every element of a homogeneous system with the molecular density n — we easily see that we can replace (7) by

$$-\frac{1}{\Theta n_x} \frac{dp_x}{dn_x} \frac{dn_x}{dz_x} = \frac{2}{\Theta} \frac{d\varepsilon_{cx}}{dz_x} .$$

This equation leads to

$$-\frac{dp_x}{dz_x} = 2n_x \frac{d\varepsilon_{cx}}{dz_x} , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The form of this relation recalls the statistical condition of equilibrium namely that the difference of pressure between two planes be equal to the force acting on the mass between these planes.

By integrating (9) from a point of the homogeneous phase (indicated by the index h) to a point of the capillary layer (index x) we find

$$p_h - p_x = 2 \int_{z_h}^{z_x} n \frac{d\varepsilon_c}{dz} dz = 2n_x \varepsilon_{cx} - 2 \int_{z_h}^{z_x} \frac{dn}{dz} \varepsilon_c dz ,$$

---

we have avoided to prove for each of the integrals $\int n \partial \frac{d^{2s} n}{d z^{2s}} dz$ separately that we can put for it $\int \partial n \left(\frac{d^{2s} n}{d z^{2s}} \right) dz$, as is done in the treatise of van der Waals—Kohnstamm p. 238.

In the paper of van der Waals this gives something accidental to the appearing of ε_x in the condition (VI). This advantage is due to the fact that the hypothesis of continuous transition and the expansion ε_x in a series have been introduced *after* the deduction of the condition (VI).

or $\varepsilon_{c\varkappa}$ is zero in the homogeneous layer. Instead of the former formula we may put

$$p_\varkappa = p_h - 2\mathfrak{n}_\varkappa \varepsilon_{c\varkappa} + 2\int\limits_{z_h}^{z_\varkappa} \frac{d\mathfrak{n}}{dz}\,\varepsilon_c\,dz \quad . \; . \; . \; . \; . \; . \; . \quad (10)$$

Introducing now for $\varepsilon_{c\varkappa}$ the series that follows from (6) and (6′) we find for the pressure

$$p_\varkappa = p_h + \mathfrak{n}_\varkappa \sum_{1}^{\infty} C_{2s} \frac{d^{2s}\mathfrak{n}_\varkappa}{dz_\varkappa^{2s}} - \frac{1}{2} C_2 \left(\frac{d\mathfrak{n}_\varkappa}{dz_\varkappa}\right)^2 - \sum_{2}^{\infty} C_{2s} \int\limits_{z_h}^{z_\varkappa} \frac{d\mathfrak{n}}{dz}\,\frac{d^{2s}\mathfrak{n}}{dz^{2s}}\,dz \; . \; (VIII)\;\text{1)}$$

It follows from the above reductions that we obtain for the pressure $p_\varkappa$

$$p_\varkappa = p_h + C_2 \left(\mathfrak{n}_\varkappa \frac{d^2\mathfrak{n}_\varkappa}{dz^2_\varkappa} - \frac{1}{2}\left(\frac{d\mathfrak{n}_\varkappa}{dz_\varkappa}\right)^2 \right) +$$

$$+ \sum_{s=2}^{s=\infty} C_{2s} \left[\sum_{\lambda=0}^{\lambda=s-1} (-1)^\lambda \frac{d^\lambda \mathfrak{n}_\varkappa}{dz_\varkappa^\lambda}\,\frac{d^{2s-\lambda}\mathfrak{n}_\varkappa}{dz^{\,2s-\lambda}} - \frac{1}{2}(-1)^s \left(\frac{d^s\mathfrak{n}_\varkappa}{dz_\varkappa^s}\right)^2 \right] \quad . \quad (VIII')$$

An approximation for $p_\varkappa$ may be obtained by breaking off the series at $s = 1$; we then find a formula, which agrees with one given by VAN DER WAALS namely

$$p_\varkappa = p_h + C_2 \left(\mathfrak{n}_\varkappa \frac{d^2\mathfrak{n}_\varkappa}{dz_\varkappa^2} - \frac{1}{2}\left(\frac{d\mathfrak{n}_\varkappa}{dz_\varkappa}\right)^2 \right) \quad . \; . \; . \quad (VIII'')$$

---

1) In order to reduce the integrals contained in the sum, we have the formula

$$\int\limits_{z_h}^{z_\varkappa} \frac{d\mathfrak{n}}{dz}\,\frac{d^{2s}\mathfrak{n}}{dz^{2s}}\,dz = \frac{d\mathfrak{n}_\varkappa}{dz_\varkappa}\,\frac{d^{2s-1}\mathfrak{n}_\varkappa}{dz_\varkappa^{2s-1}} - \int\limits_{z_h}^{z_\varkappa} \frac{d^2\mathfrak{n}}{dz^2}\,\frac{d^{2s-1}\mathfrak{n}}{dz^{2s-1}}\,dz \, .$$

Where the remaining integral may again be transformed by the same operation. In this way we are finally led to a term in which the integration may be performed namely

$$(-1)^s \int\limits_{z_h}^{z_\varkappa} \frac{d^s\mathfrak{n}}{dz^s}\,\frac{d^{s+1}\mathfrak{n}}{dz^{s+1}}\,dz = \frac{(-1)^s}{2}\left(\frac{d^s\mathfrak{n}_\varkappa}{dz_\varkappa^s}\right)^2 .$$

It follows from (VIII) together with the above reductions that by integrating from the one homogeneous phase h_1 to the other h_2 we obtain:

$$p_{h_1} = p_{h_2},$$

which is the well kwown condition for thermodynamical equilibrium.

The constant μ of the equation (VI) can be determined, if we observe that in the homogeneous phases $\varepsilon_{c\varkappa}=0$. Representing the molecular density of these phases by $\mathfrak{n}_1$ and $\mathfrak{n}_2$, we have

$$log\frac{\omega_1}{\mathfrak{n}_1}+\mathfrak{n}_1\frac{d\,log\,\omega_1}{d\,\mathfrak{n}_1}+\frac{2a\mathfrak{n}_1}{\Theta}=log\frac{\omega_2}{\mathfrak{n}_2}+\mathfrak{n}_2\frac{d\,log\,\omega_2}{d\,\mathfrak{n}_2}+\frac{2a\mathfrak{n}_2}{\Theta}=\mu, \quad . \quad (11)$$

which yields one equation between $\mathfrak{n}_1$ and $\mathfrak{n}_2$. We can find a second by means of the observation made at the end of the note of p. 534 We have

$$p_{h_1}=p_{h_2}\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where the p's are known functions of $\mathfrak{n}_1$ and $\mathfrak{n}_2$ (c.f. (8)).

After having determined $\mathfrak{n}_1$ and $\mathfrak{n}_2$ by means of the foregoing equations we can use the first to determine μ.

The thickness of the capillary layer depends on the modulus Θ, it can be determined by means of (VI); we can also calculate the number of the molecules in this layer. This number being known, the equation (I) enables us to calculate the height of the liquid and gaseous phases.

§ 5. We have now to examine whether the frequency of the system determined by (II) and (VI) is really maximum, in other terms whether the condition of the system is one of stable equilibrium. The quantity $\delta^2 log\,\zeta$ consists of three parts, the two first of which belong to the elements of the homogeneous phases h_1 and h_2, whereas the third relates to the capillary layer c.

We may put the first parts in the form

$$\delta_h{}^2\,log\,\zeta=\sum\nolimits_h\frac{\delta n_\varkappa{}^2}{2n_\varkappa}\left(-1+\frac{d}{d\mathfrak{n}_\varkappa}\left(\mathfrak{n}_\varkappa{}^2\frac{d\,log\,\omega_\varkappa}{d\,\mathfrak{n}_\varkappa}\right)+\frac{2a\mathfrak{r}_\varkappa}{\Theta}\right), \quad (VII')$$

where $\sum_h$ has to be extended over the elements of the homogeneous layers h_1 and h_2. For the part belonging to the capillary layer we have the formula

$$\delta^2{}_c\,log\,\zeta=\sum_c\frac{\delta n_\varkappa{}^2}{2n_\varkappa}\left(-1+\frac{d}{d\mathfrak{n}_\varkappa}\left(\mathfrak{n}_\varkappa{}^2\frac{d\,log\,\omega_\varkappa}{d\,\mathfrak{n}_\varkappa}\right)\right)+$$

$$+\frac{\pi\,dz}{\Theta}\sum_c\delta n_\varkappa\sum_\nu\psi(\nu dz)\,(\delta\mathfrak{n}_{\varkappa-\nu}+\delta\mathfrak{n}_{\varkappa+\nu}). \quad . \quad . \quad (VII'')$$

In order that $\delta^2\,log\,\zeta$ be negative, it is necessary that $\delta^2{}_{h_1}\,log\,\zeta$, $\delta^2{}_{h_2}\,log\,\zeta$ and $\delta^2{}_c\,log\,\zeta$ be negative for all possible values of the numbers $\delta n_\varkappa$.

The parts relating to the homogeneous layers may be written in the form

$$\delta^2_{h\alpha} \log \zeta = \left(-1 + \frac{d}{d\mathrm{n}_\alpha}\left(\mathrm{n}^2_\alpha \frac{d \log \omega_\alpha}{d\,\mathrm{n}_\alpha}\right) + \frac{2a\mathrm{n}_\alpha}{\Theta}\right) \sum_{h\alpha} \frac{\delta n^2_\varkappa}{2n_\varkappa},$$

where α is 1 or 2. These contributions are negative, if

$$-1 + \frac{d}{d\,\mathrm{n}_\alpha}\left(\mathrm{n}^2_\alpha \frac{d \log \omega_\alpha}{d\,\mathrm{n}_\alpha}\right) + \frac{2a\mathrm{n}_\alpha}{\Theta} < 0 \quad . \quad . \quad . \quad . \quad (IX)$$

Now, we can transform this condition by means of the function p (c. f. (8)). We then find as a condition for the stability

$$\frac{dp_\alpha}{d\mathrm{n}_\alpha} > 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (IX')$$

for the homogeneous phases. As for these phases, the function p_α represents the pressure, the condition (IX′) is nothing else than the known thermodynamical condition for stability.

Not only must (IX) be fulfilled, it is also necessary that $\delta^2{}_c \log \zeta$ be negative, for there are possible variations in which $\delta n_\varkappa$ is zero everywhere in the homogeneous layers.

I shall transform the first sum in $\delta^2{}_c \log \zeta$ by means of (VI). I shall write for it

$$\sum_c \frac{\delta n_\varkappa}{2} \delta\mathrm{n}_\varkappa \left(-\frac{1}{\mathrm{n}_\varkappa} + \frac{1}{\mathrm{n}_\varkappa} \frac{d}{d\mathrm{n}_\varkappa}\left(\mathrm{n}^2_\varkappa \frac{d \log \omega_\varkappa}{d\,\mathrm{r}_\varkappa}\right)\right),$$

which may be replaced by

$$\sum_c \frac{\delta n_\varkappa}{2} \delta\mathrm{n}_\varkappa \frac{d}{d\mathrm{n}_\varkappa}\left(\log \frac{\omega_\varkappa}{\mathrm{n}_\varkappa} + \mathrm{n}_\varkappa \frac{d \log \omega_\varkappa}{d\,\mathrm{n}_\varkappa}\right).$$

By a transformation of the same kind as that which leads to (7), we can replace the foregoing expression by

$$\frac{1}{\Theta} \sum_c \delta n_\varkappa \delta\mathrm{n}_\varkappa \frac{\dfrac{d\varepsilon_\varkappa}{dz_\varkappa}}{\dfrac{d\mathrm{n}_\varkappa}{dz_\varkappa}}.$$

Introducing the value of $\varepsilon_\varkappa$ by means of (5′), and considering that the differentiation of $\mathrm{n}_{\varkappa-\nu}$ with respect to $z_\varkappa$ gives the same result as that with respect to $z_{\varkappa-\nu}$, we find for the sum under consideration

$$-\frac{\pi\, dz}{\Theta} \sum_c \frac{\delta n_\varkappa\, \delta\mathrm{n}_\varkappa}{\dfrac{d\mathrm{n}_\varkappa}{dz_\varkappa}} \sum \psi\,(\nu dz) \left(\frac{d\mathrm{n}_{\varkappa-\nu}}{dz_{\varkappa-\nu}} + \frac{d\mathrm{n}_{\varkappa+\nu}}{dz_{\varkappa+\nu}}\right),$$

therefore (VII″) may be reduced to

$$\frac{\pi\, dz}{\Theta}\left\{\sum_c \delta n_\kappa \sum_\nu \psi(v\,dz)\,(\delta\mathfrak{n}_{\kappa-\nu}+\delta\mathfrak{n}_{\kappa+\nu})\,-\right.$$

$$\left.-\sum_c \frac{\delta n_\kappa\,\delta\mathfrak{n}_\kappa}{\frac{d\mathfrak{n}_\kappa}{dz_\kappa}}\sum_\nu \psi(v\,dz)\left(\frac{d\mathfrak{n}_{\kappa-\nu}}{dz_{\kappa-\nu}}+\frac{d\mathfrak{n}_{\kappa+\nu}}{dz_{\kappa+\nu}}\right)\right\}. \quad . \quad (VII''')$$

Now we can easily show that this sum is essentially negative. For this purpose we arrange the terms in the following way. From the first sum we take the term $\delta n_\kappa\, \psi(v\,dz)\, \delta\mathfrak{n}_{\kappa-\nu}$, and also the term $\delta n_{\kappa-\nu}\, \psi(v\,dz)\, \delta\mathfrak{n}_\kappa$. These are equal, and their sum is

$$\frac{2}{dz}\,\delta n_\kappa\, \delta n_{\kappa-\nu}\, \psi(v\,dz).$$

Next from the second sum we take the term

$$-\frac{\delta n_\kappa\,\delta\mathfrak{n}_\kappa\,\frac{d\mathfrak{n}_{\kappa-\nu}}{dz_{\kappa-\nu}}}{\frac{d\mathfrak{n}_\kappa}{dz_\kappa}}\,\psi(v\,dz).$$

and also the term

$$-\frac{\delta n_{\kappa-\nu}\,\delta\mathfrak{n}_{\kappa-\nu}}{\frac{d\mathfrak{n}_{\kappa-\nu}}{dz_{\kappa-\nu}}}\,\frac{d\mathfrak{n}_\kappa}{dz_\kappa}\,\psi(v\,dz).$$

Adding those four we find

$$-\frac{1}{dz}\,\frac{d\mathfrak{n}_\kappa}{dz_\kappa}\,\frac{d\mathfrak{n}_{\kappa-\nu}}{dz_{\kappa-\nu}}\left(\frac{\delta n_\kappa}{\frac{d\mathfrak{n}_\kappa}{dz_\kappa}}-\frac{\delta n_{\kappa-\nu}}{\frac{d\mathfrak{n}_{\kappa-\nu}}{dz_{\kappa-\nu}}}\right)^2\psi(v\,dz).$$

This result is essentially negative, for $\frac{d\mathfrak{n}}{dz}$ has the same sign at all points.[1]

We can arrange all the terms of (VII''') in the same way. Accordingly, the whole sum may be written as a sum of essentially negative quantities, and therefore $\delta^2_v \log \zeta$ is essentially negative. From this it follows that a system consisting of two coexisting phases with a capillary layer between them is stable, if the homogeneous phases taken by themselves are stable.

§ 6. I shall now determine the entropy and the free energy of the system considered.

Gibbs[2]) showed that Ψ, the constant in the equation (II) has the properties of the thermodynamical free energy. I shall therefore determine the quantity Ψ, which may properly be called the statistical free energy.

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[1]) A similar transformation does not hold for the elements of the homogeneous phases for there $\frac{d\mathfrak{n}}{dz}=0$.

[2]) J. W. Gibbs. Elementary principles in Statistical Mechanics 1902.

Taking the sum of the numbers ζ, obtained by giving to the numbers n all possible values, we get the total number N of the systems in the ensemble. I shall represent this sum by Σ_e, so that we have the identity

$$N=\sum_e \zeta = (2\pi\Theta m)^{\frac{3}{2}n} N e^{\frac{\Psi}{\Theta}} n! \sum_e \prod_1^k \frac{(\omega_\varkappa\, dz_k)^{n_\varkappa}}{n_\varkappa!} e^{-\frac{n_\varkappa \varepsilon_\varkappa}{\Theta}} \quad . \; (X)$$

This equation enables us to determine Ψ. In order to find the value of $\Sigma_e \zeta$, we may by means of (VII) express the frequency ζ of an arbitrary system in that ζ_0 of the system of maximum frequency. From (VII) it follows that

$$\zeta = \zeta_0 \, e^{\sum\limits_1^k \left[\frac{\delta n^2_\varkappa}{2n_\varkappa}\left(-1+\frac{d}{d\mathfrak{n}_\varkappa}\left(\mathfrak{n}^2_\varkappa \frac{d\log\omega_\varkappa}{d\mathfrak{n}_\varkappa}\right)\right) + \frac{\pi}{\Theta}\sum\limits_1^k \delta n_\varkappa \sum \psi(\nu dz)\left(\delta\mathfrak{n}_{\varkappa-\nu}+\delta\mathfrak{n}_{\varkappa+\nu}\right) dz.\right]}$$

Introducing this into the sum Σ_e, we obtain

$$\sum_e \zeta = \zeta_0 \sum_e e^{\sum\limits_1^k \left[\frac{\delta n^2_\varkappa}{2n_\varkappa}\left(-1+\frac{d}{d\mathfrak{n}_\varkappa}\left(\mathfrak{n}^2_\varkappa \frac{d\log\omega_\varkappa}{d\mathfrak{n}_\varkappa}\right)\right) + \frac{\pi}{\Theta}\sum\limits_1^k \delta n_\varkappa \sum\limits_\nu \psi(\nu dz)\left(\delta\mathfrak{n}_{\varkappa-\nu}+\delta\mathfrak{n}_{\varkappa+\nu}\right) dz.\right]}$$

In my dissertation [1]) I have shown, that this may be replaced in a fair approximation by

$$\sum_e \zeta = \zeta_0 \sum_e e^{\sum\limits_1^k -\frac{\delta n_\varkappa^2}{2n_\varkappa}} \quad . \; . \; . \; . \; . \; (13)$$

The quantity ζ_0 is given by the equation

$$\zeta_0 = \frac{N e^{\frac{\Psi}{\Theta}} n^n (2\pi\Theta m)^{\frac{3}{2}n} \sqrt{2\pi n}}{(2\pi)^{k/2}(n_1 \ldots n_\varkappa \ldots n_k)^{1/2}} \prod_1^k \left(\frac{\omega_\varkappa}{\mathfrak{n}_\varkappa}\right)^{n_\varkappa} e^{-\frac{n_\varkappa \varepsilon_\varkappa}{\Theta}} , \; . \; . \; (14)$$

---

[1]) p.p. 111 and 126.

where the numbers $n_\varkappa$ and $\mathfrak{n}_\varkappa$ have the values following from (VI).

We now have

$$\sum_e e^{\sum_1^k - \frac{\delta n_\varkappa^2}{2 n_\varkappa}} = (2\pi)^{\frac{k-1}{2}} (n_1 \ldots n_\varkappa \ldots n_k)^{1/2}\, n^{-1/2}$$

and therefore, using (13) and (14), we find for Ψ

$$e^{-\frac{\Psi}{\Theta}} = (2\pi\Theta m)^{\frac{3}{2}n}\, n^n \prod_1^k \left(\frac{\omega_\varkappa}{\mathfrak{n}_\varkappa}\right)^{n_\varkappa} e^{-\frac{n_\varkappa \varepsilon_\varkappa}{\Theta}} \quad . \quad . \quad . \quad (XI)$$

Gibbs showed that the quantity $-\bar{\eta}$ defined by the equation

$$-\bar{\eta} = \frac{\bar{\varepsilon} - \Psi}{\Theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (XII)$$

has the proporties of the entropy s. Here the quantity $\bar{\varepsilon}$ is the average energy in the canonical ensemble; it is equal to the energy of the system of maximum frequency [1].

The kinetic energy of this system amounts to

$$\frac{3}{2}\, n\, \Theta\, .$$

For the potential energy we have written

$$\sum_1^k n_\varkappa\, \varepsilon_\varkappa\, ,$$

and the value of $\bar{\varepsilon}$ is therefore

$$\bar{\varepsilon} = \frac{3}{2}\, n\, \Theta + \sum_1^k n\ \varepsilon_\varkappa\, .$$

For s we have the equation

$$s = \frac{3}{2}\, n + \frac{3}{2}\, n \log\,(2\,\pi\,\Theta\, m) + n \log n + \sum_1^k n_\varkappa \log \frac{\omega}{\mathfrak{n}_\varkappa}$$

$$= Const + \frac{3}{2}\, n \log \Theta + \sum_1^k n_\varkappa \log \frac{\omega_\varkappa}{\mathfrak{n}_\varkappa}$$

$$= Const + \frac{3}{2}\, n \log \Theta + \int_0^Z \mathfrak{n} \log \frac{\omega}{\mathfrak{n}}\, dz. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (XIII)$$

---

[1] Gibbs showed that the average energy in an ensemble is equal to the most common energy in that ensemble. Now not every system with this energy is equivalent to the system of maximum frequency, but the most common energy is equal to the energy of the latter system therefore the same is true for the average energy. This result may also be obtained by determining $\bar{\varepsilon}$ directly by means of (VII).

This formula can be used to determine s, if we know the manner in which n depends on z. We easily see from (XIII), that, just as VAN DER WAALS supposed, the entropy in each element of volume depends only on the density n and on the number of collisions in that element[1]. We could expect this, having found exactly the same condition of equilibrium to which his theory leads.

It must, however, not been forgotten that the whole above development and therefore the hypothesis of VAN DER WAALS are only valid, if the assumptions about the attractive forces introduced at p. 526 and 527 are true. The changes that will have to be made in the theory, when these assumptions are relinquished, must be a matter of further examination[2].

7. Finally I shall determine the force exerted in a horizontal direction by the system. Consider a system identical with the former; only let the section be no longer equal to unit of area, but let it be o. It is easily seen that this has no influence at all on the former developments. The density $\mathrm{n}_\varkappa$ and the energy $\varepsilon_\varkappa$ are determined by analogous equations; the only difference is that $n_\varkappa$ (the number of molecules in the layer $dz_\varkappa$,) is now given by $\mathrm{n}_\varkappa \, o \, dz_\varkappa$. instead of by $\mathrm{n}_\varkappa \, dz_\varkappa$.

For Ψ we have therefore the formula

$$-\frac{\Psi}{\Theta} = Const. + \sum_{1}^{k} o\,\mathrm{n}_\varkappa \left(log \frac{\omega_\varkappa}{\mathrm{n}_\varkappa} - \frac{\varepsilon_\varkappa}{\Theta} \right) dz_\varkappa =$$

$$= Const. + o \int_{0}^{Z} \mathrm{n} \left(log \frac{\omega}{\mathrm{n}} - \frac{\varepsilon}{\Theta} \right) dz \quad . \quad . \quad . \quad . \quad . \quad (15)$$

The average component, corresponding to the parameter o, of the force exerted by the systems of the ensemble is given — as GIBBS showed — by the relation

$$\overline{K_0} = -\frac{d\Psi}{do} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (XIV)$$

The force K_0, exerted by the systems of maximum frequency, is equal to the average force $\overline{K_o}$. Therefore equation (XIV) may be used to determine the force in a real system. Before I use (15) to determine K_0, I shall put this equation in a new form by means of (VI) namely

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[1] The function ω is connected with this number.

[2] In this examination the function $\vartheta\,(n_\varkappa, dz_\varkappa)$ introduced in my dissertation will have to play a part.

$$-\frac{\Psi}{\Theta} = Const. + o\int_0^Z\left(\mu\mathrm{n} - \mathrm{n}^2\frac{d\log\omega}{d\mathrm{n}} - \frac{a\mathrm{n}^2}{\Theta} + \frac{\mathrm{n}\varepsilon_c}{\Theta}\right)dz =$$

$$= Const. + (\mu-1)\,n + o\int_0^Z\left((\mathrm{n}-\mathrm{n}^2\frac{d\log\omega}{d\mathrm{n}} - \frac{a\mathrm{n}^2}{\Theta} + \frac{\mathrm{n}\varepsilon_c}{\Theta}\right)dz.$$

with the aid of (10) we can replace this formula by

$$-\frac{\Psi}{\Theta} = C' + \frac{o}{\Theta}\int_0^Z p_h dz + \frac{o}{\Theta}\int_0^Z\left(-\mathrm{n}\varepsilon_c + 2\int_{z_h}^{z}\frac{d\mathrm{n}}{dz}\varepsilon_c dz\right)dz \quad . \ (XI')$$

For K_0 we get finally

$$K_0 = p_h Z + \int_0^Z\left(-\mathrm{n}\varepsilon_c + 2\int_{z_h}^{z}\frac{d\mathrm{n}}{dz}\varepsilon_c\, dz\right)dz \quad . \quad . \quad . \quad (XV)$$

An approximate value for K_0 can be found, by putting $\varepsilon_{c_z} = -\frac{C_2}{2}\frac{d^2\mathrm{n}_z}{dz^2_z}$.

This value for K_0 amounts to

$$K_0 = p_h Z + \frac{C_2}{2}\int_0^Z\left(\mathrm{n}\frac{d^2\mathrm{n}}{dz^2} - \left(\frac{d\mathrm{n}}{dz}\right)^2\right)dz =$$

$$= p_h Z - C_2\int_0^Z\left(\frac{d\mathrm{n}}{dz}\right)^2 dz$$

$$= p_h Z + C_2\int_0^z \mathrm{n}\frac{d^2\mathrm{n}}{dz^2}dz \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

When the surface of the capillary layer increases by unit of area the free energy (so far as it depends on capillary action) decreases by

$$\int_0^Z\left(-\mathrm{n}\varepsilon_c + 2\int_{z_h}^{z}\frac{d\mathrm{n}}{dz}\varepsilon_c dz\right)dz \quad . \quad . \quad . \quad . \quad , \quad . \quad (17)$$

or, if we use the approximate values by

$$- C_2 \int_0^Z \left(\frac{d\mathrm{n}}{dz}\right)^2 dz =$$

$$+ C_2 \int_0^Z \mathrm{n} \frac{d^2\mathrm{n}}{dz^2} dz \; , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (18)$$

i. e. the free energy increases proportionally to the surface. Only the elements of the capillary layer contribute to the integrals, for it is only in these elements that ε_c and $\frac{d\mathrm{n}}{dz}$ differ from zero. The quantities expressed by (17) and (18), taken with the negative sign, agree with what is commonly called the capillary energy. In this form they also represent the so called surface tension.

The quantity

$$p_h - \mathrm{n}_\varkappa \varepsilon_{c\varkappa} + 2 \int_{z_h}^{z_\varkappa} \frac{d\mathrm{n}}{dz} \varepsilon_c dz ,$$

or the corresponding approximate quantity (c. f. (16))

$$pZ + \frac{C_2}{2}\left(\mathrm{n}_\varkappa \frac{d^2\mathrm{n}_\varkappa}{dz^2_\varkappa} - \left(\frac{d\mathrm{n}_\varkappa}{dz_\varkappa{}^2}\right)^2\right) ,$$

may be called the horizontal pressure in the element $dz_\varkappa$ at the height $z_\varkappa$. I shall represent it by $p_{t\varkappa}$. As we can see from (10), the connection between $p_\varkappa$ and $p_{t\varkappa}$ is given by the formula

$$p_{t\varkappa} - p_\varkappa = \mathrm{n}_\varkappa \, \varepsilon_{c\varkappa} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (XVI)$$

The term $\varepsilon_{c\varkappa}$ being 0 in the homogeneous layer, we have

$$p_{t\varkappa} = p_\varkappa = p_{h1} = p_{h2} .$$

We can determine the sign of $\varepsilon_{c\varkappa}$, and therefore that of $p_{t\varkappa} - p$, by means of the equations (VI) and (10). We then come to a discussion exactly analogous to that which VAN DER WAALS has given on p. 19 of his paper [1]).

If one goes upward from the liquid phase, ε_c is first 0, then positive, then 0 again, after that negative and finally 0 in the gaseous phase.

By means of the foregoing considerations, we can obtain all the results formerly found by VAN DER WAALS and the above method may also be applied to a spherical mass, whose density is distributed symmetrically around the centre.

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[1]) C.f. VAN DER WAALS—KOHNSTAMM p. 239.

Mathematics. — "*On fourdimensional nets and their sections by spaces.*" (Fourth part). By Prof. P. H. SCHOUTE.

The net (C_{24}).

1. In the first communication under this title we have transformed the net of the cells $C_8^{(2)}$ into a net (C_{24}) in two different ways, into a net of cells $C_{24}^{(2)}$ and into a net of cells $C_{24}^{(\sqrt{2})}$. The difference between these two transformations may be characterized by the remark, that each cell $C_{24}^{(2)}$ contains as a part the cell $C_8^{(2)}$ from which it is derived, whilst it is possible to consider each cell $C_{24}^{(\sqrt{2})}$ to be bodily inscribed in a cell $C_8^{(2)}$ by starting from *two* nets of $C_8^{(2)}$, each of which fills the space Sp_4 entirely, related to one another in such a way, that the system of the vertices of the cells of the one is at the same time the system of the centres of the cells of the other and reversely. As we have used the second of these transformations in the deduction of the table of relations between the axes inserted in the first paper, we still cling to it here, though it cannot be denied that the advantage of including the cells $C_{24}^{(\sqrt{2})}$ in boxes $C_8^{(2)}$ is not quite so important as was that of including the cells $C_{16}^{(2\sqrt{2})}$ in cells $C_8^{(2)}$, $C_8^{(4)}$, all cells $C_{24}^{(\sqrt{2})}$ of the net corresponding with one another in orientation.

We again restrict ourselves to the sections of the net (C_{24}) by spaces normal to one of the four different kind of axes of one of the cells $C_{24}^{(\sqrt{2})}$ and therefore of all the cells of the net. We remember to that end that the table on page 544 quoted above indicates which diameters of the box $C_8^{(2)}$ correspond to the chosen axes OE_{24}, OK_{24}, OF_{24}, OR_{24} of $C_{24}^{(\sqrt{2})}$. We repeat here the part of it relating to the net (C_{24}) in the form

$$OE_{24}=\overset{(4)}{OF_8},\quad OK_{24}=(2,1,\overset{(8)}{1},0)C_8,\quad OF_{24}=\overset{(3)}{OK_8}=(3,1,\overset{(6,7)}{1},1)C_8,\quad OR_{24}=\overset{(5)}{OR_8}=\overset{(1,2)}{OE_8},$$

indicating by means of the figures (4), (8), . . . , (5), (1,2) between brackets the lines of the table, where these results are to be found. By this it is immediately evident, that the series of sections normal to OE_{24} and to OK_{24} involve every time a definite position of the intersecting space with respect to the axes of the including cells $C_8^{(2)}$, whilst this position can be chosen in two different manners in the cases of the two other series. This gives rise to six different series of parallel sections of a $C_{24}^{(\sqrt{2})}$ enclosed in a $C_8^{(2)}$, which have to be considered in the following.

2. We adopt here the method followed in the second and third papers and indicate the results of the determination of the section of a cell $C_{24}^{(\sqrt{2})}$ in two ways. Once more the first plate gives us the projection of the limiting elements of the cell $C_{24}^{(\sqrt{2})}$ on the diameter normal to the intersecting space, and the characteristics of the sections deduced tabularly from these projections; in this only four series of sections present themselves. The second plate shows further the form of the sections in parallel perspective, enclosed in the circumscribed eightcell; here we have to deal with six different series. Finally a third plate principally contains some diagrams with three-dimensional space-fillings generated by the intersection of the net, whilst the third of these diagrams numbered separately, which dominates the deduction of the projections of plate I, has been transferred thither, in order to facilitate comparison. We now proceed to the consideration of the diagrams 1 and 2 of plate III.

The manner in which the cell $C_{24}^{(\sqrt{2})}$ is inscribed in the box $C_8^{(2)}$ is characterized by this, that the vertices of $C_{24}^{(\sqrt{2})}$ are the centres of the faces of $C_8^{(2)}$. We indicate how these points combine themselves by twos to extrimeties of edges, by threes to vertices of faces and by sixes to vertices of limiting octahedra, by indicating these octahedra in the diagrams 1 and 2. It is immediately clear that eight of these 24 octahedra are polarly inscribed in the eight limiting cubes of $C_8^{(2)}$; fig. 1 exhibits two opposite faces $ABC, A'B'C'$ of one of these octahedra, whilst fig. 2 shows two opposite faces $ABC, A''B''C''$ of one of the sixteen remaining octahedra. Indeed the vertices of $C_{24}^{(\sqrt{2})}$ divide themselves with respect to the space of a limiting cube of $C_8^{(2)}$, the central space parallel to it, and the space of the opposite limiting cube into three groups of 6, 12, 6 points and the central section is evidently the combination (12, 24, 14) of cube and octahedron in equilibrium; from this can be deduced that the *second* limiting octahedron of which ABC is a face has for opposite face one of the two faces of this combination parallel to ABC and then — it goes without saying — the triangular face differing in orientation from ABC. So we get indeed sixteen new octahedra, each of the eight triangular faces $A''B''C''$ of the combination (12, 24, 14) procuring two of them.

The projections given under the headings OE_{24}, OK_{24}, OF_{24}, OR_{24} on plate I can be easily deduced from plate I of the second paper by means of the projections of the faces and limiting bodies of the including eightcell given there. By tracing the centres of all these faces and the octahedra polarly inscribed in all these limiting cubes we obtain the results tabulated in the four diagrams 3^a, 3^b, 3^c, 3^d of plate I, i. e. in the cases OE_{24}, OK_{24} only eight, in the cases OF_{24}, OR_{24} only sixteen of the 24 limiting octahedra. As the laws of reciprocity require that the arrangement of the 24 limiting octahedra into groups for the cases OE_{24}, OK_{24}, OF_{24}, OR_{24} corresponds to that of the 24 vertices for the cases OR_{24}, OF_{24}, OK_{24}, OE_{24} respectively, the obtained numbers (2, 4, 2), etc. of the octahedra can be completed to the really occurring numbers (6, 12, 6) added between brackets. Then from the projections of vertices and octahedra those of edges and faces are easily deduced.

3. We now proceed to the consideration of the sections represented on plate II in parallel perspective; of these the sections of the $C_{24}^{(\sqrt{2})}$ have been derived from the tables of the plate I, whilst those of the enveloping $C_8^{(2)}$ have been taken from the second paper.

This plate is divided by three heavy vertical lines into four parts successively concerned with sections normal to OE_{24}, to OK_{24}, to OF_{24}, to OR_{24}. Of these parts the third and the fourth are subdivided into two parts, in relation to the two possible positions of the circumscribed eightcell.

Sections normal to $OE_{24} = OF_8$.

If we restrict ourselves here to the sections of transition and the intermediate sections bisecting the distances between these, we have to deal with five cases corresponding to the fractions $0, \frac{1}{8}, \frac{2}{8}, \frac{3}{8}, \frac{4}{8}$.

As to the circumscribed $C_8^{(2)}$ we then find a rectangular parallelopipedon, the base of which is a square with side 2, whilst the height is successively 0, $\frac{1}{2}\sqrt{2}$, $\sqrt{2}$, $\frac{3}{2}\sqrt{2}$, $2\sqrt{2}$ and as to $C_{24}^{(\sqrt{2})}$ we get a point, a cube with edge $\frac{1}{2}\sqrt{2}$, a cube with edge $\sqrt{2}$, a polyhedron (32, 48, 18) limited by 6 squares and 12 hexagons with two axes of symmetry — which may be characterized as a rhombic dodecahedron truncated at the octahedral vertices by the faces of a cube — and this semiregular polyhedron itself (24, 36, 14) with one kind of face, which is also called granatohedron [1]).

Sections normal to $OK_{24} = (2, 1, 1, 0)\ C_8$.

Here we have to distinguish two series of fractions, one related to the C_{24} itself, the other related to the box C_8. The fractions $0, \frac{1}{12}, \frac{2}{12}, \ldots, \frac{6}{12}$ placed below on the right hand correspond to the seven sections in the first case, whilst the fractions $\frac{2}{16}, \frac{3}{16}, \ldots, \frac{8}{16}$ placed above at the left hand present themselves in the second case.

In our second paper we have explained why the problem of the determination of the section of an eightcell loses one dimension in the case $(2, 1, 1, 0)\ C_8$ and all the sections are prisms with height 2, the bases of which are the sections of a cube with a series of parallel planes normal to the line connecting the origin with the point $(2, 1, 1)$, i.e. of planes determining segments proportional to $\frac{1}{2}, 1, 1$ on the axis of coordinates. For the seven cases presenting themselves here fig. 4 indicates the form of the bases; so it is not difficult to draw the prisms represented in the second column of plate II. As it is not quite so easy to deduce from the characteristics given on plate I the forms of the sections of C_{24}, the faces of these sections situated in the boundary of the prisms have been determined independently by means of the diagrams 5^a, 5^b, 5^c closely connected to fig. 4. If we suppose that OX_1, OX_2, OX_3, OX_4 (fig. 4) are the four edges of the eightcell concurring in O and that the intersecting space is brought parallel to OX_4 through the seven sections of the cube, it is clear that this space will be cut by the space $O(X_1\ X_2\ X_3)$ in a plane parallel to the endplanes of the prism, by the two spaces $O(X_1\ X_2\ X_4)$ and $O(X_1\ X_3\ X_4)$ in planes parallel to the couples of parallel lateral faces of the middle section, by the space $O(X_2\ X_3\ X_4)$ in a plane not presenting itself in the middle section that — according to its position in our figures — may be called the face behind. We now try to find in each of these four spaces of coordinates a plane normal to the indicated plane of intersection of that space with the intersecting space, on to which moreover the projection of the limiting cube situated in that space of coordinates and the octahedron polarly inscribed in it is as simple as possible. So we get in $O(X_1\ X_2\ X_3)$ the plane $O(X_1\ Y)$, in $O(X_1\ X_2\ X_4)$ the plane $O(X_1\ X_2)$, in $O(X_1\ X_3\ X_4)$ the plane $O(X_1\ X_3)$, in $O(X_2\ X_3\ X_4)$ the plane $O(X_2\ X_3)$. With omission of the case $O(X_1\ X_2\ X_3)$ equal to that of $O(X_1\ X_2\ X_4)$ these projections are represented in the diagrams 5^a, 5^b, 5^c where the series of parallel intersecting planes are indicated by their parallel traces. For any position of the intersecting plane the required sections of the octahedra are easily found by means of these diagrams. So the section pqr of the octahedron in the lozenge os of fig. 5^a is the hexagon of the endplanes and the section $p'q'r'$ of the octahedron in the rectangle $o'r'$ of fig. 5^b is the deltoid of the lateral faces, of the middle section, whilst the section $p''q''r''s''$ of the octahedron in the rectangle $o''t''$ furnishes to us the hexagon in the face behind of the section corresponding to the fractions $\frac{1}{12}$ and $\frac{3}{12}$. With the aid of the characteristics of the sections tabulated on plate I we then easily find how the visible faces of the section are to be completed to the total boundary of the polyhedron by means of faces situated within the prism.

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[1]) Here too the vertices of the faces of the section of $C_{24}^{(\sqrt{2})}$ visible in the limiting faces of the section of $C_8^{(\sqrt{2})}$ have been brought to the fore; the shaded faces passing into one another by a parallel translation of the intersecting space are shaded in the same way.

The form of the polyhedral sections of C_{24} obtained in this manner is rather complicated and therefore not easily described; all the forms admit of two common characteristic features: they possess an axis with the period 3, in our figures the horizontal line MN, and four planes of symmetry, three through the axis and one normal to it. This axis MN is no axis for the prismal section of the circumscribed C_8, the middle section excepted; for this section it is an axis with the period 2 and in connection with this it becomes an axis with the period 6 for the middle section of C_{24} that admits of seven planes of symmetry.

It is easily verified that the length of the axis MN within the seven different sections is successively

$\sqrt{2}$, $\frac{7}{6}\sqrt{2}$, $\frac{8}{6}\sqrt{2}$, $\frac{9}{6}\sqrt{2}$, $\frac{10}{6}\sqrt{2}$, $\frac{11}{6}\sqrt{2}$ and $2\sqrt{2}$.

Sections normal to $OF_{24} = OK_8$.

To the five polyhedra presenting themselves here — see the first column of the third part of plate II — correspond below to the right the fractions 0, $\frac{1}{8}, \ldots, \frac{4}{8}$, above to the left the fractions $\frac{2}{12}$, $\frac{3}{12}, \ldots, \frac{6}{12}$.

Here too the problem of the determination of the section of the eightcell has lost one dimension, these sections being prisms with a height 2, the bases of which are sections of a cube, this time normal to a diagonal. Here too it is desirable to determine independently the faces of the sections of the inscribed C_{24} situated in the limiting faces of these prisms. To this end we have to revert to the diagrams 5^a, 5^b, 5^c and to replace the series of parallel lines representing the traces of the intersecting planes normal to the planes of the diagrams made up in the supposition of the intersecting space (2,1,1,0) by those which are connected with the simpler supposition (1, 1, 1, 0). As the new diagrams 5^b and 5^c become equal to one another, the new series of parallel lines have only been indicated — by dotted lines — in the diagrams 5^a and 5^b. So we find — entirely in the manner explained above — the section $u\,v\,w$ of the octahedron in the equiangular semiregular hexagon $t\,x$ forming the end planes, the section $t'\,u'\,v'\,w'$ in the rectangle $s'\,x'$ forming the three lateral faces of the prismal section corresponding to the fraction $\frac{5}{12}$; so we easily get — once more in the same manner as above — by means of the data of plate II the total boundary of each of the five sections of C_{24}.

The forms obtained in this way possess the same characteristic properties as those of the preceding group, an axis MN with the period 3 and four planes of symmetry for the excentric sections, an axis with the period 6 and seven planes of symmetry for the central section. We can only record this difference that here the line MN is an axis for the sections of the C_{24} and those of the circumscribed C_8 together, and that its length within the polyhedra always remains 2.

Sections normal to $OF_{24} = (3, 1, 1, 1)\ C_8$.

Here we find — see the second column of the third part of plate II

— the five sections of C_{24} already obtained, but enclosed now in parts of rhombohedra, regularly truncated at one of the axial vertices[1]), and — as far as the middle section is concerned — enclosed in an unmutilated rhombohedron. For these sections of the circumscribed eightcell one may compare plate II of our second paper.

Here too the sections of C_{24} and C_8 correspond principally with one another with respect to axis and planes of symmetry. Only the plane bisecting the axis MN perpendicularly is not a plane of symmetry for the truncated rhombohedra and the axis maintains its period 3 for the unmutilated one.

Sections normal to $OR_{24} = OR_8$.

In this simplest case partially mentioned above we find — see the upper region of the fourth part of plate II — corresponding successively to the fractions $0, \frac{1}{4}, \frac{2}{4}$ the octahedron, the semiregular polyhedron (24, 36, 14) with one kind of vertex, and the combination (12, 24, 14) of cube and octahedron in equilibrium, always enclosed in an invariable cube.

Sections normal to $OR_{24} = OE_8$.

Here the three sections once more must be characterized by pairs of fractions, below to the right $0, \frac{1}{4}, \frac{2}{4}$ related to C_{24}, above to the left $\frac{2}{8}, \frac{3}{8}, \frac{4}{8}$ related to C_8.

The three sections of C_{24} found above reappear here — see the lower region of the fourth part of plate II — successively inscribed in a tetrahedron, a semiregular polyhedron (12, 18, 8) with one kind of vertex, and an octahedron, represented in their turn inscribed in cubes for the more simple deduction of the true measures.

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[1]) These rhombohedra bounded by lozenges with acute angles of 84°15′39″ are represented in toto, the section with the truncating plane being indicated by heavy lines.

In arranging the sections on plate II I mistook the sections of the C_8 occurring here for cubes, though I myself had indicated their true nature in the second paper. After having read the manuscript Mrs. A. Boole Stott had the goodness to set me right as to the text; but the diagrams could no more be corrected. Happily the difference between these cubes and the slightly elongated cubes that should replace them is hardly perceptible.

4. From the two ways mentioned in the preceding paper leading to the knowledge of the threedimensional space-fillings generated by the intersection of the net (C_{24}) we choose here the more theoretical one, in which is deduced from the section of the intersecting space with a definite cell C_{24} how this space must affect the other cells C_{24}. To this end we indicate in diagram 6 how the boxes $C_8^{(2)}$ filling twice the space Sp_4 project themselves on the chosen axes OE_{24}, OK_{24}, OF_{24}, OR_{24}. Of the projections on the axes OF_8, $(2, 1, 1, 1)\ C_8$, OK_8, OR_8 1) coinciding with the named ones the third case OK_8 distinguishes itself from the other by this that the centre of the eightcell (2, 6, 6, 2) does not project itself in the projection of a vertex; in connection with this each space-filling corresponding to OK_8 deviates from the general rule according to which the difference of the fractions corresponding to sections partaking in a selfsame space-filling is itself a fraction with numerator unity, the denominator of which is equal to the number of equal parts of the projection of an eightcell. So according to this rule this difference is $\frac{1}{2}$ in the first and the fourth case, $\frac{1}{4}$ in the third case of the fig. 6, and it *would* have been $\frac{1}{3}$ in the case of OK_8, but *is* now only $\frac{1}{6}$.

Now we have indicated in general which sections of C_{24} must generate together a space-filling we can proceed to the treatment of the individual cases; we shall then see that in any of these combinations of sections each face occurs twice in the same position, as the juxtaposition of the pieces requires.

Space-fillings normal to OE_{24}. Here we have to deal successively with the combinations of fractions $\left(0, \frac{4}{8}\right)$, $\left(\frac{1}{8}, \frac{5}{8}\right)$, $\left(\frac{2}{8}, \frac{6}{8}\right)$; so we find three space-fillings, that of granatohedra, that of granatohedro truncated at the six octahedral vertices and of small cubes, that of cubes with edges twice as long.

Space-fillings normal to OK_{24}. Expressed in the fractions belonging to C_8 here the combinations $\left(0, \frac{4}{16}, \frac{8}{16}, \frac{12}{61}\right)$, $\left(\frac{1}{16}, \frac{5}{16}, \frac{9}{16}, \frac{13}{16}\right)$, $\left(\frac{2}{16}, \frac{6}{11}, \frac{10}{16}, \frac{14}{16}\right)$ present themselves; as no threedimensional section

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1) In order to make the diagrams fit better on the plate, the order of succession is changed there by interchanging $(2, 1, 1, 0)\ C_8$ and OK_8.

of C_{24} corresponds to $0, \frac{1}{16}, \frac{2}{16}$ these symbols, difference in orientation being disregarded, may be reduced to $\left(\frac{4}{16}, \frac{8}{16}\right), \left(\frac{5}{16}, \frac{9}{16}, \frac{13}{16}\right), \left(\frac{6}{16}\right)$. We now consider each of these cases separately.

Case $\left(\frac{4}{16}, \frac{8}{16}\right)$. In this space-filling the middle section (26, 42, 18) with the fraction $\frac{8}{16}$ occurs in one orientation only, whilst the polyhedron (11, 18, 9) with the fraction $\frac{4}{16}$ occurs in two different positions passing into one another by a rotation of 180° about the axis MN with the period 3. In order to make this space-filling perfectly clear we project it successively on a plane normal to the common direction of the axes and on one of the axes. These projections can be found immediately, if we know how the composing polyhedra are to be put in contact with each other. Therefore we indicate first that two polyhedra of different form in facial contact with each other have always a deltoid in common, whilst this contact can be realized for two polyhedra (11, 18, 9) by a lozenge only, for two polyhedra (26, 42, 18) by a hexagon only; this is clear if we bear in mind that all the axes MN are parallel.

The projection of the space-filling on to a plane normal to the axes MN may be regarded as the superposition to one another of two wellknown plane-fillings (fig. 7^a), that of regular hexagons and that of equilateral triangles, the vertices of the polygons of the one being the centres of the polygons of the other and vice versa. If this space-filling is cut by a plane bisecting an axis MN normally the result is the plane-filling by triangles or that by hexagons according as that axis belongs to the form (11, 18, 9) or to the form (26, 42, 18).

The projection of the space-filling on to an axis is given in fig. 8^a in two layers of which the upper one is related to the axes of the central section, the one below to the axes of the polyhedra (11, 18, 9). The axes MN of the first group with the length $2\sqrt{2}$ fill the whole line, whilst the axes $M'N'$ of the second group with the length $\frac{4}{3}\sqrt{2}$ leave parts of the line uncovered. On one axis of both groups the projections of the vertices of the polyhedron have been indicated, on MN the points A, B, C, D, on $M'N'$ the points

A', B', C'' ; of these C, D, N coincide respectively with N', A', B[1]).

Case $\left(\frac{3}{16}, \frac{7}{16}, \frac{11}{16}\right)$. Each of the three forms (14, 21, 9), (26, 39, 15), (32, 48, 18) with the fractions $\frac{3}{16}, \frac{5}{16}, \frac{7}{16}$ occurs in two oppositely orientated positions. The shape of the faces proves that two polyhedra $\left(\frac{5}{16}\right)$ in contact *must* have an isosceles trapezium in common and two polyhedra $\left(\frac{7}{16}\right)$ a hexagon of the equatorial belt, whilst the required parallelism of all the axes MN only allows the *possibility* of two polyhedra $\left(\frac{3}{16}\right)$ having a hexagon, and two polyhedra $\left(\frac{5}{16}\right)$ having a hexagon of the equatorial belt in common. Moreover the contact of a polyhedron $\left(\frac{5}{16}\right)$ and a polyhedron $\left(\frac{7}{16}\right)$ *must* find place in an equatorial hexagon, that of the forms $\left(\frac{3}{16}\right)$ and $\left(\frac{7}{16}\right)$ in a deltoid, whilst the forms $\left(\frac{3}{16}\right)$ and $\left(\frac{5}{16}\right)$ *may* be in contact by a hexagon.

From all this may be easily deduced that the projection of the space-filling on a plane normal to the axes (fig. 7^b) consists in the superposition of two plane-fillings, of which the one brought to the fore here contains equatorial sections of the polyhedra $\left(\frac{3}{16}\right)$ and $\left(\frac{5}{16}\right)$, whilst the more regular one of hexagons, the vertices of which coincide with the centres of the polygons of the former, is built up of equatorial sections of the polyhedron $\left(\frac{7}{16}\right)$. This proves at the same time that no two polyhedra $\left(\frac{3}{16}\right)$ are in facial contact, neither that two polyhedra $\left(\frac{5}{16}\right)$ have a hexagon in common.

The projection on an axis is represented in fig. 8^b in three layers, successively related to the polyhedra $\left(\frac{7}{16}\right)$, $\left(\frac{5}{16}\right)$, $\left(\frac{3}{16}\right)$. In none of the three layers do these axes cover the line of projection entirely. In the manner explained above have been indicated on MN the projections $A, B, \ldots, H$, on $M'N'$ the projections A', B', ..., F', on $M''N''$ the projections $A'', B'', \ldots, D''$ of vertices; here the pairs and triples (E, M'), (F, M''), (G, A', A''), (H, B', B''), (N, C'') coincide.

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[1] These points have been indicated by the same letters on the polyhedra corresponding to $\frac{8}{16}$ and $\frac{11}{16}$ on the second part of plate II; but here the dashes have been omitted.

Case $\left(\frac{6}{16}\right)$. In this case of the unique polyhedron (14, 24, 12) occurring in two opposite orientations, bounded by an equatorial belt of six isosceles trapezia and two polar regions of triples of lozenges, the contact of the polyhedra takes place either by an isosceles trapezium or by a lozenge.

The projection on a plane normal to the axes consists in the plane-filling of regular hexagons, each of these hexagons divided in the same way into three lozenges.

The projection on an axis (fig 8^c) consists of two layers; all axes MN, $M'N'$ have the same length. By the projections A, B, C, D of the vertices each axis is divided into five equal parts; the last two segments CD, DN of MN cover the first two segments $M'A'$, $A'B'$ of $M'N'$.

If we consider the portion of the space-filling situated between the two planes normal to the plane of the diagram (fig. 8) according to a and b and if we imagine that the halves of the polyhedra (14, 24, 12) lying between these planes are hollow, we have before us a figure in space, imitating very nearly the shape of the honey-comb of the beehive. Indeed a space-filling, the polyhedra of which really are double beecells has been described by A. ANDREINI 1). But the space-filling derived here from fourdimensional space does not characterize itself by the known minimum property of the beecell; it is rather closely connected with the space-filling by granatohedra. If we divide a granatohedron in two equal halves by a plane normal to a diagonal and rotate one of the halves an angle of 180° about that diagonal, we generate a polyhedron also limited by six isosceles trapezia and six lozenges, but the trapezia have another shape.

Space-fillings normal to OF_{24}. Expressed in the fractions belonging to the sections of C_8 we have to deal here with the two combinations $\left(0, \frac{2}{12}, \frac{4}{12}, \ldots, \frac{10}{12}\right)$, $\left(\frac{1}{12}, \frac{3}{11}, \ldots, \frac{11}{12}\right)$ which may be reduced to $\left(\frac{4}{12}, \frac{6}{12}\right)$ and $\left(\frac{3}{12}, \frac{5}{12}\right)$.

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1) In ANDREINI's memoir "Sulle reti di poliedri regolari e semiregolari e sulle corrispondenti reti correlative" (*Memorie della Società italiana delle Scienze*, series 3, volume 14, p. 75—129, 1905) the three dodecahedra filling space are treated in the paragraphs 76, 77, 87. For the rest my study has nothing of any importance in common with his work, which is nicely illustrated by stereoscopic views of threedimensional space-fillings.

Case $\left(\frac{4}{12}, \frac{6}{12}\right)$. Of the two polyhedra (12, 21, 11), (18, 30, 14) corresponding to $\left(\frac{4}{12}\right)$, $\left(\frac{6}{12}\right)$ only the first one occurs in two opposite orientations. The facial contact of two forms (12, 21, 11) takes place by a triangle, that of two forms (18, 30, 14) by a hexegon and that of two polyhedra of different shape by a trapezium.

The projection on a plane normal to the axes is represented in fig. 9^a. In the three shaded hexagons $ABCDEF$ one recognizes immediately the upper planes of three central sections $\left(\frac{6}{12}\right)$ and in LMN the base, in $F_1E_1B_2A_2D_3C_3$ the equatorial section of the body $\left(\frac{4}{12}\right)$ lying between, etc.

Case $\left(\frac{3}{12}, \frac{5}{12}\right)$. Here both forms (18, 27, 11) and (30, 45, 17) occur in two different orientations. Two polyhedra (18, 27, 11) of the same orientation have no face in common, two polyhedra (18, 27, 11) of different orientation in contact have a hexagon in common, so as to make their axes one another's production. Contact of two polyhedra (30, 45, 17) takes place either by a semiregular hexagon or by a hexagon with two axes of symmetry in a plane inclined with respect to the axes, according as the two polyhedra correspond or differ in orientation. Contact by a hexagon with two axes situated in a plane parallel to the axes MN takes place between two polyhedra of different shape.

The projection of the space-filling normal to the axes MN is represented in fig. 9^b. In the three shaded semiregular hexagons drawn in toto one recognizes easily the three upper planes of the section $\frac{5}{12}$, in the other shaded parts of the figure portions of lower planes of the section $\left(\frac{5}{12}\right)$ in opposite orientation, in the two larger semiregular hexagons partially covering one another in the centre of the figure equatorial sections of the form $\left(\frac{3}{12}\right)$, for which the thickness, i. e. the segment on the axis lying within the polyhedron, is half as large as that of $\left(\frac{5}{12}\right)$, etc.

Space-fillings normal to OR_{21}. Finally we get here two known space-fillings, that of octahedra and combinations of cube and octahedron in equilibrium, and that of the body (24, 36, 14) of Lord KELVIN.

Geophysics. — *"On the duration of showers at Batavia."* By Dr. J. P. VAN DER STOK.

Since January 1st 1866 hourly observations of different meteorological quantities have been made at the Batavia Observatory and also of the rainfall so that, at present, a series of 40 years is available comprising some 25000 rainy hours distributed over about 8200 showers.

In less favourable climates it is not practicable to have such observations made continuously night and day and, as self-registering instruments are subject to frequent interruptions, this series may be regarded as a unique material for investigation.

The purpose of this inquiry is to investigate the distribution of showers of variable duration in different seasons, and to apply to these frequencies suitable frequency-formulae.

A rainy hour is defined as every hour during which rain fell, if it were only 0.1 m.m.; the duration of a shower is defined as the number of subsequent hours in which rain was observed: e.g. by a shower of 10 hours' duration we do not assume incessant rain during this period, but that no hour has passed without some rain having fallen.

As during the first decade no observations were made on Sundays, the total amount of hours e.g. for January is not equal to:

$$40.31.24 = 29760$$

but to:

$$(40.31-44)\,24 = 28704.$$

The results of this inquiry have been summarized in Table I.

Average values of quantities so divergent and intermittent as rainfall are hardly sufficient to convey an adequate idea of the way in which this phenomenon affects the climate and it is questionable whether excessive quantities or durations are to be included in the computation, because even the mean values deduced from a long series of observations may be affected to an important degree by one shower and thus the meaning which we attach to averages, loses its value.

Consequently the frequencies given in Table II give not only a more complete, but also a more accurate idea of this climatological factor than the average values of Table I.

From this summary it appears that in April, almost suddenly, the condition of rainfall shows an alteration such, that the probability of showers of long duration is considerably reduced; in the next months this probability again increases whilst in August the distribution

TABLE I. Showers at Batavia, 1866—1905.

	Number of hours	Number of rainy hours	Percent. of rainy hours	Number of showers	Mean dur. of showers in hours	Mean numb. of showers per diem
January....	28704	4456	15.5	1367	3.26	1.14
February....	26136	4565	17.5	1251	3.65	1.15
March......	28680	3026	10.5	939	3.22	0.79
April	27792	1704	6.1	664	2.57	0.57
May.......	28680	1138	4.0	428	2.66	0.36
June..	27768	1222	4.4	405	3.02	0.34
July........	28728	924	3.2	341	2.71	0.28
Augustus ...	28680	516	1.8	212	2.43	0.18
September..	27768	897	3.2	324	2.77	0.28
October	28704	1219	4.2	480	2.54	0.49
November ..	27768	2039	7.3	709	2.88	0.61
December ..	28704	3372	11.7	1071	3.15	0.90
Year........	338112	25078	7.42	8190	3.06	0.58

shows some resemblance to that of April. The phenomenon of rainfall, therefore, is subject to an annual variation consisting of a single period as shewn by the percentage of the showers and a semi-annual period with minima in April and August. Further it appears from Table II that showers of 24 consecutive hours rarely occur (14 cases in 8190), but that, although very rarely, showers of 100, 109 and even of 147 hours have been observed in February and March.

2. Besides the numerical representation as given in Table II, also an analytical representation is of some importance as, in the constants calculated, peculiarities of the curve of distribution often occur which appear neither in the numerical, nor in a graphic representation and, at the same time, these constants can be considered as a quantitative measure of these peculiarities.

In treating frequencies of this kind, the number of constants to be used must remain restricted to a few, as every constant necessitates the computation of an average of higher order and constants based on high moments will, in this case, be practically idle.

It seems, therefore, desirable not to introduce more than two

TABLE II.

Frequencies of duration of showers at Batavia, 1866—1905.

Dur. in hours	Jan.	Febr.	Mrch	Apr.	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
1	417	357	277	220	137	112	115	80	89	152	221	316
2	321	263	254	185	121	115	89	55	96	154	193	273
3	206	203	138	110	71	55	62	36	65	86	126	175
4	130	126	89	59	38	46	26	16	32	30	52	111
5	81	77	59	43	26	33	13	10	12	27	33	64
6	51	60	45	17	10	14	13	7	11	13	34	33
7	51	43	23	14	12	9	7	4	6	10	12	25
8	33	29	13	12	6	7	10	3	5	—	13	20
9	17	22	13	3	2	6	2	—	3	2	9	14
10	16	20	5	1	2	2	1	1	2	—	3	8
11	10	14	5	—	2	2	—	—	1	3	5	9
12	9	6	5	—	1	—	—	—	—	1	2	4
13	4	9	2	—	—	2	1	—	1	1	—	4
14	5	6	2	—	—	1	2	—	1	—	1	—
15	4	2	1	—	—	—	—	—	—	—	3	5
16	6	1	—	—	—	—	—	—	—	—	—	3
17	1	3	1	—	—	—	—	—	—	—	1	—
18	—	4	2	—	—	—	—	—	—	—	—	1
19	1	1	1	—	—	—	—	—	—	—	—	1
20	1	1	—	—	—	—	—	—	—	—	—	1
21	—	—	—	—	—	—	—	—	—	—	—	1
22	—	—	1	—	—	—	—	—	—	—	—	—
23	—	—	—	—	—	—	—	—	—	—	1	—
24	1	1	—	—	—	—	—	—	—	—	—	1
25	1	1	1	—	—	—	—	—	—	—	—	—
26	—	—	—	—	—	—	—	—	—	—	—	1
27	—	—	—	—	—	1	—	—	—	—	—	—
28	—	—	1	—	—	—	—	—	—	—	—	—
29	—	—	—	—	—	—	—	—	—	—	—	—
30	—	—	—	—	—	—	—	—	—	—	—	—
31	—	—	—	—	—	—	—	—	—	—	—	—
32	—	—	—	—	—	—	—	—	—	—	—	1
33	1	—	—	—	—	—	—	—	—	—	—	—
100	—	1	—	—	—	—	—	—	—	—	—	—
109	—	1	—	—	—	—	—	—	—	—	—	—
147	—	—	1	—	—	—	—	—	—	—	—	—
Total	1367	1251	939	664	428	405	341	212	324	480	709	1071

constants in the formulae, so that no average values higher than those of the second order need to be calculated and, as the phenomenon presents an annual and a semi-annual variation, it is reasonable to expect that this number will be sufficient to arrive at a suitable expression for the law of distribution.

Then, in the first place, the frequency-formula known as Type III of Prof. PEARSON's formulae finds an application.

As the quantities under consideration are rainy hours, with the exclusion of hours in which no rain has fallen, the function must vanish for $x = 0$ if we take the duration zero for origin of coordinates, then for increasing values of x the function will rapidly rise to a maximum-value and decrease in a continuous way without any definite limit.

In this case PEARSON's Type III assumes the form:

$$u = \mathfrak{A}\, e^{-mx}\, x^{p} \quad \ldots\ldots\ldots \quad (1)$$

If we put

$$mx = z$$

the expression for the mean of the n^{th} order becomes:

$$\mu_n = \frac{\mathfrak{A}}{m^{p+n+1}} \int_0^\infty e^{-z}\, z^{p+n}\, dz$$

and

$$\mu_0 = \frac{\mathfrak{A}}{m^{p+1}} \int_0^\infty e^{-z}\, z^{p}\, dz = \frac{\mathfrak{A}\, \Gamma(p+1)}{m^{p+1}} = 1$$

from which we find for the determination of the two constants m and p the expressions:

$$m = \frac{\mu_1}{\mu_2 - \mu_1^2} \text{ en } p + 1 = \frac{\mu_1^2}{\mu_2 - \mu_1^2} . \quad \ldots\ldots \quad (2)$$

$\mathfrak{A}$ being defined so that the area of the curve becomes equal to unity, this quantity must not be regarded as a characteristic of the curve.

Applying these formulae to the frequencies of Table II, we find the values given in Table III.

In computing the means it is to be noted that the duration of a shower of say 3 hours is not to be regarded as a duration between 2.5 and 3.5 hours, but as a mean duration of 2.5 hours, because any duration beyond 3 hours would transfer the quantity into the 4 hours group. Further it must be noted that for February and March the excessive durations of 100 and more hours have been excluded from the calculation.

TABLE III. Constants of PEARSON'S formula, Type III.

	$\mathfrak{A}$	m	p
January	0.3249	0.357	0.163
February	0.3073	0.365	0.273
March	0.3483	0.400	0.227
April	0.6441	0.854	1.194
May	0.5575	0.731	0.941
June	0.3921	0.486	0.466
July	0.4863	0.600	0.625
August	0.6829	0.832	1.022
September	0.5044	0.677	0.876
October	0.5443	0.648	0.646
November	0.4129	0.491	0.413
December	0.3344	0.359	0.131

3. In the second place we have to consider the formula in series form given by the author in a former publication [1]) for the case that the function must vanish for $x = 0$:

$$u = \Sigma A'_n \psi'_{n+1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and, if the mean of the n^{th} order is represented by:

$$\mu_n = \int\limits_0 u x^n \, dx$$

$$A'_n = \frac{\mu_n}{0!(n+1)!n!} - \frac{\mu_{n-1}}{1!n!(n-1)!} + \frac{\mu_{n-2}}{2!(n-1)!(n-2)!} \cdots \frac{(-1)^n}{n!}. \quad (4)$$

We may now introduce a suitable alteration of the scale value by multiplying form. (3) by the factor h and further writing everywhere xh for x and $\mu_n h^n$ for μ_n.

$$A'_0 = \mu_0 = 1$$

$$A'_1 = \frac{\mu_1 h}{2!1!} - \mu_0 = \frac{\mu_1 h}{2} - 1$$

$$A'_2 = \frac{\mu_2 h^2}{3!2!} - \frac{\mu h}{2!1!} + \frac{1}{2!} \text{ etc.}$$

---

[1]) These proceedings Vol X (799—817).

As by the use of these formulae the function and its integral assume rather large and the A-coefficients small values, it is desirable to divide the function by $(n+1)!$ and to multiply the A-coefficients with the same factor, then:

$$u = \Sigma A_n \psi_{n+1}$$

$$A_n = A'_n (n+1)!$$

$$(n+1)! \psi_{n+1} = \psi'_{n+1}$$

$$A_0 = 1$$

$$A_1 = \mu_1 h - 2$$

$$A_2 = \frac{\mu_2 h^2}{2!} - \frac{3\mu_1 h}{1!} + 3$$

$$A_3 = \frac{\mu_3 h^3}{3!} - \frac{4\mu_2 h^2}{2!} + \frac{6\mu_1 h}{1!} - 4 \text{ etc.}$$

The constant h may then be determined by putting:

$$A_1 = 0$$

from which:

$$h = \frac{2}{\mu_1}$$

and

$$A_2 = \frac{2\mu_2}{\mu_1^2} - 3 = \frac{2\mu_2 - 3\mu_1^2}{\mu_1^2}.$$

TABLE IV. Constants of the series-formula.

	h	A_2
January	0.613	0.7206
February	0.573	0.5714
March	0.651	0.6292
April	0.778	—0.0893
May	0.752	0.0297
June	0.662	0.3640
July	0.738	0.2301
August	0.823	—0.0119
September	0.722	0.0652
October	0.787	0.2154
November	0.694	0.4148
December	0.635	0.7669

Table IV exhibits the values of the constants h and A_2 as calculated by means of these formulae.

Either formula gives a good image of the characteristic differences of the curve in the course of the year, viz. the sudden transition in April, the congruity between the curves for April and August and the single and double annual variations in the phenomenon.

If we define as normal the curve obtained by putting $p = 1$ in PEARSON's formula and $A_2 = 0$ in the series-formula, both formulae assume the form:

$$u = Ae^{-xh}\, x$$

and we see from Tables III and IV that in the East-monsoon the curve approaches the normal form; in April, May, August and September its shape is almost fully normal, but in June and July the curve clearly shows considerable deviations from this simple type.

Peculiarities of this kind are not perceptible in the *rainfall* during these months at Batavia, but in some other places, more directly exposed to the influence of the South-East-monsoon as Tjilatjap, a rather large increase of rainfall obtains after April, thus giving rise to a secondary maximum. In the West-monsoon the deviations from the normal type are greatest.

4. Owing to the rather large irregularities in the data, the monthly frequencies as given in Table II are not very suitable to serve as material for putting frequency-formulae to the test of a comparison between observed and calculated aggregate values; for this purpose, therefore, all frequencies for the period April to November have been taken together and reduced to a total of 1000. (Table V).

In the last column of this Table frequencies are given between the limits x and 0, which frequencies are to be compared to the corresponding values calculated from the formula:

$$B = \int_0^x u\,dx$$

For the constants of the formulae we find:

$$h = 0.9141 \qquad \mathfrak{A} = 0.5366$$

$$A_2 = 0.6429 \qquad m = 0.5576$$

$$p = 0.2222$$

The integration of the series-formulae between the limits x and

TABLE V.
Frequencies of duration of showers, April – November.

Durat. in hours	I	II	III
1	1126	316	316
2	1008	283	599
3	611	172	771
4	299	84	855
5	197	55	910
6	119	34	944
7	74	21	965
8	56	16	981
9	27	8	989
10	12	3	992
11	13	4	996
12	4	1	997
13	5	1	998
14	5	1	999
15	3	1	1000
16	—		
17	1		
18	—		
19	—		
20	—		
21	—		
22	1		
23	1		
Total	3562	1000	

a offers no difficulties; from the differential equation of the ψ function it follows that:

$$B_{n+1} = \int_0^x \psi_{n+1}\, dx = - \frac{x^2 e^{-x}}{(n+1)!} \cdot \frac{1}{n} \frac{dT''_n}{dx}$$

Introducing the factor h we find:

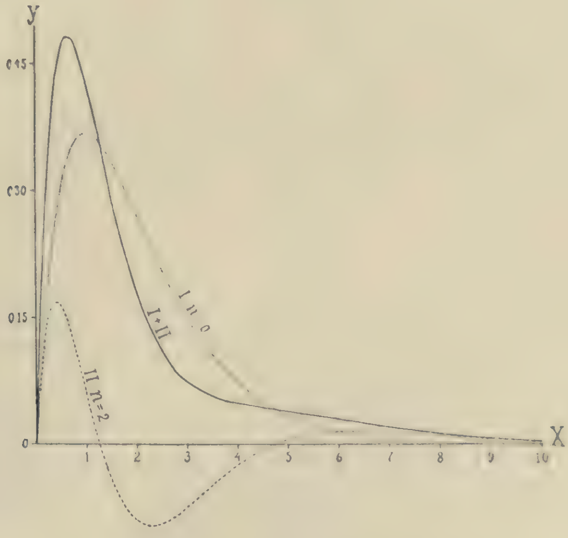
$$B_1 = 1 - (1 + xh)\, e^{-xh}$$

$$B_2 = -\frac{x^2h^2}{2!}\, e^{-xh}$$

$$B_3 = -\frac{x^3h^3}{3!}\, e^{-xh} - B_2$$

$$B_4 = -\frac{x^4h^4}{4!}\, e^{-xh} - 2\, B_3 - B_2 \quad \text{etc.}$$

Values of these integrals are given in Table VIII and corresponding values of the function in Table VII. The figure shows how a frequency-curve (full line), as represented by the ψ functions, is constructed out of its components (broken line) for the case that both h and A_2 are equal to unity, which does not differ much from the conditions which obtain at Batavia during the dry season.



The integration between fixed limits of formula (1), Type III, is very laborious; substituting:

$$m\, x = z$$

we find by development:

$$\int_0^z u\,dz = \frac{\mathfrak{A}}{m^{p+1}}\,\frac{z^{p+1}}{p+1}\left[1 - \frac{p+1}{p+2}\, z + \frac{p+1}{p+3}\,\frac{z^2}{2!} - \text{etc.}\right].$$

Owing to its feeble convergency, this expression is of no practical use for values of z greater than 3.

In SCHLÖMILCH'S Compendium, 2te Aufl. p. 261 in the chapter "Unvollständige Gammafunctionen" the way is indicated to transform this expression into a much stronger converging series:

$$\mathfrak{A}\int_0^x e^{-mx}\, x^p\, dx = 1 - \frac{\mathfrak{A}e^{-x}}{m^{p+1}}\Bigg[x^p - \frac{p}{\lambda}\left\{1 - \frac{a_1}{x+1} + \frac{a_2}{(x+1)(x+2)} - \text{etc.}\right\}$$

where, in our case, $\lambda = 1 - p = 0.7778$ and

$a_1 = \lambda = 0.7778$ $\quad a_3 = \lambda^3 + \lambda = 1.2484$

$a_2 = \lambda^2 = 0.6050$ $\quad a_4 = \lambda^4 + 4\lambda^3 - \lambda = 2.0082$

$a_5 = \lambda^5 + 10\lambda^3 - 5\lambda^2 + 8\lambda = 8.1881.$

The results of this investigation are summarized in Table VI.

TABLE VI.

Observ.		Calc. series			Calc. Type III	Observ. — Calc.	
		A_0B_0	A_2B_2	Total		Series	Type III
1	316	232.7	74.9	307.6	321.9	8	— 6
2	599	545.4	67.5	612.9	581.3	—14	18
3	771	758.9	13.4	772.3	746.5	— 1	24
4	855	879.7	—24.3	855.4	848.2	0	7
5	910	941.0	—36.4	904.6	909.8	5	0
6	944	973.1	—33.2	939.9	946.7	4	— 3
7	965	987.7	—24.8	962.9	968.6	2	— 4
8	981	994.5	—16.5	978.0	981.6	3	— 1
9	989	997.5	—10.1	987.4	989.2	2	0
10	992	998.9	— 5.9	993.0	993.7	— 1	— 2
11	996	999.5	— 3.3	996.2	996.3	0	0
12	997	999.8	— 1.8	998.0	997.9	— 1	— 1
13	998	999.9	— 0.93	999.0	998.8	— 1	— 1
14	999	999.96	— 0.48	999.48	999.28	0	0
15	1000	999.98	— 0.24	999.74	999.58	0	0

TABLE VII. Values of the function ψ_{n+1}.

x	$n=0$	$n=1$	$n=2$	$n=3$	$n=4$
0.0	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	0.0905	−0.0860	0.0816	−0.0774	0.0732
0.2	0.1638	−0.1474	0.1321	−0.1097	0.1046
0.3	0.2223	−0.1889	0.1589	**−0.1320**	**0.1079**
0.4	0.2681	−0.2145	**0.1680**	−0.1280	0.0937
0.5	0.3033	−0.2275	0.1643	−0.1121	0.0697
0.6	0.3293	**−0.2305**	0.1515	−0.0892	0.0412
0.7	0.3476	−0.2260	0.1327	−0.0628	0.0121
0.8	0.3595	−0.2157	0.1102	−0.0355	−0.0151
0.9	0.3659	−0.2013	0.0860	−0.0090	−0.0388
1.0	**0.3679**	−0.1839	0.0613	0.0153	−0.0583
1.1	0.3662	−0.1648	0.0372	0.0368	−0.0731
1.2	0.3614	−0.1446	0.0145	0.0549	−0.0834
1.3	0.3543	−0.1240	−0.0065	0.0696	−0.0894
1.4	0.3452	−0.1036	−0.0253	0.0809	**−0.0916**
1.5	0.3347	−0.0837	−0.0418	0.0889	−0.0905
1.6	0.3230	−0.0646	−0.0560	0.0939	−0.0866
1.7	0.3106	−0.0466	−0.0678	**0.0962**	−0.0805
1.8	0.2975	−0.0298	−0.0774	0.0961	−0.0728
1.9	0.2842	−0.0142	−0.0848	0.0940	−0.0638
2.0	0.2707	0.0000	−0.0902	0.0902	−0.0541
2.1	0.2572	0.0129	−0.0939	0.0851	−0.0429
2.2	0.2438	0.0244	−0.0959	0.0789	−0.0340
2.3	0.2306	0.0344	**−0.0965**	0.0719	−0.0241
2.4	0.2178	0.0436	−0.0958	0.0645	−0.0147
2.5	0.2052	0.0513	−0.0941	0.0566	−0.0059
2.6	0.1931	0.0579	−0.0914	0.0487	0.0022
2.7	0.1815	0.0635	−0.0880	0.0409	0.0100
2.8	0.1703	0.0681	−0.0840	0.0332	0.0159
2.9	0.1596	0.0718	−0.0795	0.0257	0.0215
3.0	0.1494	0.0747	−0.0747	0.0187	0.0261
3.1	0.1397	0.0768	−0.0696	0.0121	0.0300
3.2	0.1304	0.0783	−0.0644	0.0059	0.0329
3.3	0.1217	0.0791	−0.0590	0.0003	0.0352
3.4	0.1135	**0.0794**	−0.0537	−0.0048	0.0366
3.5	0.1057	0.0793	−0.0484	−0.0094	0.0375
3.6	0.0984	0.0787	−0.0433	−0.0134	**0.0377**
3.7	0.0915	0.0778	−0.0383	−0.0169	0.0375
3.8	0.0850	0.0765	−0.0334	−0.0199	0.0368
3.9	0.0789	0.0750	−0.0288	−0.0217	0.0356
4.0	0.0733	0.0733	−0.0244	−0.0244	0.0342
4.1	0.0680	0.0714	−0.0203	−0.0260	0.0325
4.2	0.0630	0.0693	−0.0164	−0.0273	0.0306
4.3	0.0584	0.0671	−0.0127	−0.0281	0.0285
4.4	0.0540	0.0648	−0.0094	−0.0287	0.0263
4.5	0.0500	0.0625	−0.0063	**−0.0289**	0.0242
4.6	0.0462	0.0601	−0.0034	−0.0289	0.0217
4.7	0.0428	0.0577	−0.0008	−0.0286	0.0194
4.8	0.0395	0.0553	0.0016	−0.0281	0.0171
4.9	0.0365	0.0529	0.0037	−0.0275	0.0148

TABLE VII (continued).

x	$n=0$	$n=1$	$n=2$	$n=3$	$n=4$
5.0	0.0337	0.0506	0.0056	—0.0266	0.0126
5.1	0.0311	0.0482	0.0073	—0.0257	0.0106
5.2	0.0287	0.0459	0.0088	—0.0247	0.0086
5.3	0.0265	0.0437	0.0101	—0.0236	0.0067
5.4	0.0244	0.0415	0.0112	—0.0224	0.0049
5.5	0.0225	0.0393	0.0122	—0.0212	0.0033
5.6	0.0207	0.0373	0.0130	—0.0199	0.0018
5.7	0.0191	0.0353	0.0136	—0.0187	0.0004
5.8	0.0176	0.0334	0.0142	—0.0174	—0.0009
5.9	0.0162	0.0315	0.0146	—0.0161	—0.0020
6.0	0.0149	0.0298	0.0149	—0.0149	—0.0030
6.5	0.0098	0.0220	**0.0151**	—0.0091	—0.0063
7.0	0.0064	0.0160	0.0138	—0.0045	**—0.0074**
7.5	0.0042	0.0114	0.0119	—0.0012	—0.0070
8.0	0.0027	0.0081	0.00 8	0.0008	—0.0059
8.5	0.0017	0.0056	0.0079	0.0022	—0.0045
9.0	0.0011	0.0039	0.0061	0.0026	—0.0031
9.5	0.0007	0.0027	0.0047	**0.0027**	—0.0020
10.0	0.0005	0.0018	0.0035	0.0026	—0.0011
10.5	0.0003	0.0012	0.0026	0.0023	—0.0004
11.0	0.0002	0.0008	0.0019	0.0019	0.0000
11.5	0.0001	0.0006	0.0013	0.0016	0.0003
12.0	0.0001	0.0004	0.0010	0.0013	0.0004
12.5	0.0000	0.0002	0.0007	0.0010	**0.0005**
13.0	—	0.0002	0.0005	0.0008	0.0005
13.5	—	0.0001	0.0003	0.0006	0.0004
14.0	—	0.0001	0.0002	0.0004	0.0004
14.5	—	0.0001	0.0002	0.0003	0.0003
15.0	—	0.0000	0.0001	0.0002	0.0003
15.5	—	—	0.0001	0.0002	0.0002
16.0		—	0.0001	0.0001	0.0002
16.5	—	—	0.0000	0.0001	0.0001
17.0	—	—	—	0.0001	0.0001
17.5	—	—	—	0.0000	0.0001
18.0	—	—	—	—	0.0001
18.5	—	—	—	—	0.0000

TABLE VIII. Values of the Integral B_{n+1}.

x	$n=0$	$n=1$	$n=2$	$n=3$	$n=4$
0.0	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	0.0047	—0.0045	0.0044	—0.0042	0.0041
0.2	0.0175	—0.0164	0.0153	—0.0143	0.0133
0.3	0.0369	—0.0333	0.0300	—0.0269	0.0241
0.4	0.0616	—0.0536	0.0465	—0.0400	0.0343
0.5	0.0902	—0.0758	0.0632	—0.0521	0.0425
0.6	0.1219	—0.0988	0.0790	—0.0622	0.0481
0.7	0.1558	—0.1217	0.0933	—0.0699	**0.0507**
0.8	0.1912	—0.1438	0.1054	—0.0748	0.0505
0.9	0.2275	—0.1647	0.1153	—**0.0770**	0.0478
1.0	0.2642	—0.1839	0.1226	—0.0766	0.0429
1.1	0.3040	—0.2014	0.1276	—0.0740	0.0363
1.2	0.3374	—0.2169	0.1301	—0.0694	0.0285
1.3	0.3732	—0.2303	**0.1305**	—0.0631	0.0198
1.4	0.4082	—0.2417	0.1289	—0.0556	0.0107
1.5	0.4422	—0.2510	0.1255	—0.0471	0.0016
1.6	0.4751	—0.2584	0.1206	—0.0379	—0.0073
1.7	0.5068	—0.2640	0.1144	—0.0284	—0.0157
1.8	0.5372	—0.2678	0.1071	—0.0188	—0.0234
1.9	0.5663	—0.2700	0.0990	—0.0092	—0.0302
2.0	0.5940	—**0.2707**	0.0902	0.0000	—0.0361
2.1	0.6204	—0.2700	0.0810	0.0088	—0.0410
2.2	0.6454	—0.2681	0.0715	0.0170	—0.0449
2.3	0.6692	—0.2652	0.0619	0.0245	—0.0478
2.4	0.6915	—0.2613	0.0523	0.0314	—0.0498
2.5	0.7127	—0.2565	0.0428	0.0374	—0.0508
2.6	0.7326	—0.2511	0.0335	0.0427	—**0.0509**
2.7	0.7513	—0.2450	0.0245	0.0472	—0.0504
2.8	0.7689	—0.2384	0.0159	0.0509	—0.0491
2.9	0.7854	—0.2314	0.0077	0.0538	—0.0472
3.0	0.8009	—0.2240	0.0000	0.0560	—0.0448
3.1	0.8153	—0.2165	—0.0072	0.0575	—0.0420
3.2	0.8288	—0.2087	—0.0139	0.0584	—0.0389
3.3	0.8414	—0.2008	—0.0201	**0.0587**	—0.0354
3.4	0.8532	—0.1929	—0.0257	0.0585	—0.0318
3.5	0.8641	—0.1850	—0.0308	0.0578	—0.0281
3.6	0.8743	—0.1771	—0.0354	0.0567	—0.0244
3.7	0.8838	—0.1692	—0.0395	0.0551	—0.0206
3.8	0.8926	—0.1615	—0.0431	0.0533	—0.0169
3.9	0.9008	—0.1539	—0.0462	0.0512	—0.0133
4.0	0.9084	—0.1465	—0.0488	0.0488	—0.0098
4.1	0.9155	—0.1393	—0.0511	0.0463	—0.0064
4.2	0.9220	—0.1323	—0.0529	0.0437	—0.0033
4.3	0.9281	—0.1255	—0.0544	0.0409	—0.0003
4.4	0.9337	—0.1188	—0.0555	0.0380	0.0024
4.5	0.9389	—0.1125	—0.0563	0.0352	0.0049
4.6	0.9437	—0.1064	—0.0567	0.0323	0.0072
4.7	0.9482	—0.1005	—0.0569	0.0294	0.0093
4.8	0.9523	—0.0948	—**0.0569**	0.0266	0.0111
4.9	0.9561	—0.0894	—0.0566	0.0238	0.0127

TABLE VIII (continued).

x	$n=0$	$n=1$	$n=2$	$n=3$	$n=4$
5.0	0.9596	—0.0842	—0.0562	0.0211	0.0140
5.1	0.9628	—0.0793	—0.0555	0.0184	0.0151
5.2	0.9658	—0.0746	—0.0547	0.0159	0.0162
5.3	0.9686	—0.0701	—0.0538	0.0135	0.0169
5.4	0.9711	—0.0659	—0.0527	0.0112	0.0175
5.5	0.9734	—0.0618	—0.0515	0.0090	0.0179
5.6	0.9756	—0.0580	—0.0503	0.0070	0.0182
5.7	0.9776	—0.0544	—0.0489	0.0050	**0.0183**
5.8	0.9794	—0.0509	—0.0475	0.0032	0.0182
5.9	0.9811	—0.0477	—0.0461	0.0016	0.0181
6.0	0.9827	—0.0446	—0.0446	0.0000	0.0178
6.5	0.9887	—0.0318	—0.0371	—0.0060	0.0154
7.0	0.9927	—0.0223	—0.0298	—0.0093	0.0119
7.5	0.9953	—0.0156	—0.0233	—0.0107	0.0083
8.0	0.9970	—0.0107	—0.0179	**—0.0107**	0.0050
8.5	0.9981	—0.0074	—0.0135	—0.0100	0.0024
9.0	0.9988	—0.0050	—0.0100	—0.0088	0.0005
9.5	0.9992	—0.0034	—0.0073	—0.0074	—0.0008
10.0	0.9995	—0.0023	—0.0053	—0.0061	—0.0015
10.5	0.9997	—0.0015	—0.0038	—0.0048	—0.0019
11.0	0.9998	—0.0010	—0.0027	—0.0038	**—0.0020**
11.5	0.9999	—0.0007	—0.0019	—0.0029	—0.0019
12.0	0.9999	—0.0004	—0.0013	—0.0022	—0.0017
12.5	1.0000	—0.0003	—0.0009	—0.0017	—0.0015
13.0	—	—0.0002	—0.0006	—0.0012	—0.0012
13.5	—	—0.0001	—0.0004	—0.0009	—0.0010
14.0	—	—0.0001	—0.0003	—0.0007	—0.0008
14.5	—	—0.0001	—0.0002	—0.0005	—0.0007
15.0	—	0.0000	—0.0001	—0.0003	—0.0005
15.5	—	—	—0.0001	—0.0002	—0.0004
16.0	—	—	—0.0001	—0.0002	—0.0003
16.5	—	—	0.0000	—0.0001	—0.0002
17.0	—	—	—	—0.0001	—0.0002
17.5	—	—	—	—0.0001	—0.0001
18.0	—	—	—	0.0000	—0.0001
18.5	—	—	—	—	—0.0001
19.0	—	—	—	—	0.0000

Mathematics. — *"On curves of order four with two flecnodal points or with two biflecnodal points."* By Prof. JAN DE VRIES.

1. The points of a binodal curve of order four, C_4, are projected out of the two double points O_1 and O_2 by two pencils in correspondence (2 , 2).

So such a C_4 is determined by the relation

$$a_{22}\lambda^2\mu^2 + a_{21}\lambda^2\mu + a_{20}\lambda^2 + a_{12}\lambda\mu^2 + a_{11}\lambda\mu + a_{10}\lambda + a_{02}\mu^2 + a_{01}\mu + a_{00} = 0,$$

where

$$\lambda = x_1 : x_3 \quad \text{and} \quad \mu = x_2 : x_3 .$$

According to a well-known property the eight singular rays (λ)

are in four ways projective to the eight singular rays (μ); consequently through O_1 and O_2 pass four conics bearing each four points of intersection of two tangents out of O_1 and O_2 and at the same time four points of intersection of rays out of O_1 and O_2 to the points of contact of those tangents (double-rays of the (2 , 2)).

If O_1O_2 is a branchray for both pencils, one of the four conics degenerates, in which case C_4 has cusps in O_1 and O_2 (see my paper "*On bicuspidal curves of order four*", Proceedings of the meeting of Dec. 24th 1908, Vol. IX, p. 499).

We suppose that O_1O_2 is conjugate as double-ray to the branchrays O_1O_3 and O_2O_3. The equation of correspondence must then furnish for $\lambda = 0$ and for $\mu = 0$ the equations $\mu^2 = \infty$ and $\lambda^2 = \infty$; hence $a_{20} = 0$, $a_{02} = 0$, $a_{10} = 0$, $a_{01} = 0$.

The equation of C_4 can now be written in the form

$$x_1{}^2x_2{}^2 + 2x_1x_2x_3\,(b_1x_1 + b_2x_2 + b_3x_3) + x_3{}^4 = 0.$$

In each of the two double points one of the branches has an inflectional point; the corresponding tangents are $x_1 = 0$ and $x_2 = 0$.

Out of each of the two *flecnodal points* three more tangents can be drawn to C_4. They are represented by

$$b_1{}^2x_1{}^3 + 2b_1b_3x_1{}^2x_3 + (b_3{}^2-1)\,x_1x_3{}^2 - 2b_2x_3{}^3 = 0,$$
$$b_2{}^2x_2{}^3 + 2b_2b_3x_2{}^2x_3 + (b_3{}^2-1)\,x_2x_3{}^2 - 2b_1x_3{}^3 = 0.$$

By eliminating $x_3{}^3$ we find

$$(b_1{}^3x_1{}^3 - b_2{}^3x_2{}^3) + 2b_3x_3\,(b_1{}^2x_1{}^2 - b_2{}^2x_2{}^2) + (b_3{}^2-1)\,x_3{}^2\,(b_1x_1 - b_2x_2) = 0.$$

So on the right line $b_1x_1 = b_2x_2$ lie three points of intersection of the tangents out of O_1 with the tangents out of O_2. We shall indicate it by h.

It is evident that these three points and the point O_3 are the branchpoints for the two collocal series of points in correspondence (2,2), determined by the pencils (O_1) and (O_2) on the line h. So according to a well-known property this (2,2) is involutory.

Indeed, we find out of

$$\lambda^2\,\mu^2 + 2\,b_1\,\lambda^2\,\mu + 2\,b_2\,\lambda\,\mu^2 + 2\,b_3\,\lambda\,\mu + 1 = 0$$

and

$$b_1\,\lambda = b_2\,\mu',$$

that the (2,2) is indicated on h by the symmetric relation

$$b_2{}^2\,\mu^2\,\mu'^2 + 2\,b_1\,b_2{}^2\,(\mu^2\,\mu' + \mu\,\mu'^2) + 2\,b_1\,b_2\,b_3\,\mu\,\mu' + b_1{}^2 = 0$$

between the rays projecting it out of O_2.

2. If Q, Q' is a pair of the involutory (2,2) on h, then the points $P_1 = (O_1Q,\, O_2Q')$ and $P_2 = (O_1Q',\, O_2Q)$ lie on C_4. The line P_1P_2

intersects O_1O_2 in a point H, separated harmonically by the line h from O_1 and O_2.

So the pairs of points P_1, P_2 form on C_4 a *fundamental involution* F_2, of which each ray through H contains two pairs.

The coincidences of F_2 are the points of contact of the tangents out of $H (y_1 = b_2, y_2 = -b_1, y_3 = 0)$. The polar curve of H has as equation

$$(b_1 x_1 - b_2 x_2)(x_1 x_2 + x_3 b_x) = 0,$$

so it consists of the line h and the conic

$$x_1 x_2 + x_3 b_x = 0.$$

The points of intersection of this conic with C_4,

$$x_1^2 x_2^2 + 2 x_1 x_2 x_3 b_x + x_3^4 = 0,$$

lie on $x_3^2 = 0$ and on $x_3^2 = b_x^2$.

By combining

$$b_x = \pm x_3$$

with the equation of C_4 we find $(x_1 x_2 \pm x_3^2)^2 = 0$. So H is the point of intersection of two double tangents.

The points of contact of these double tangents forming two pairs of F_2 and being generated by the conics $x_1x_2 \pm x_3^2 = 0$, the supposition is at hand that F_2 can also be determined by means of the pencil of conics

$$x_1 x_2 = \varrho x_3^2.$$

Indeed, the movable points of intersection of these conics with C_4 lie on the rays

$$(1 + \varrho^2) x_3 + 2 \varrho b_x = 0,$$

passing through H, whilst the line h,

$$b_1 x_1 = b_2 x_2,$$

is the polar of H with respect to each conic

$$x_1 x_2 = \varrho x_3^3.$$

Resuming we can say:

Of a C_4 with two flecnodal points O_1 and O_2 two double tangents meet on the connecting line O_1O_2 of the double points. The points of contact of the four tangents which it is possible still to draw out of their point of intersection to C_4 lie on a right line, which contains moreover three points of intersection of the tangents r_1, s_1, t_1 out of O_1 with the tangents r_2, s_2, t_2 out of O_2 and the point of intersection of the inflectional tangents f_1 and f_2 in O_1 and O_2.

3. From $(f_1\, r_1\, s_1\, t_1) = (f_2\, r_2\, s_2\, t_2)$ follows

$$(f_1\, r_1\, s_1\, t_1) = (r_2\, f_2\, t_2\, s_2) = (s_2\, t_2\, f_2\, r_2) = (t_2\, s_2\, r_2\, f_2).$$

By this three conics $\varrho_2, \sigma_2, \tau_2$ through O_1 and O_2 are determined containing in succession the quadruplets of points

$$f_1r_2 \; , \; r_1f_2 \; , \; s_1t_2 \; , \; t_1s_2 \; ;$$
$$f_1s_2 \; , \; r_1t_2 \; , \; s_1f_2 \; , \; t_1r_2 \; ;$$
$$f_1t_2 \; , \; r_1s_2 \; , \; s_1r_2 \; , \; t_1f_2 \, .$$ [1])

On these too the pencils (O_1) and (O_2) arranged in (2, 2) determine involutory (2,2), which then again are connected with *fundamental involutions* on C_4. The pairs of such an involution lie on rays through the pole R, S, T of O_1O_2 with respect to the corresponding conic $\varrho_2, \sigma_2, \tau_2$. This pole is the point of intersection of two double tangents; this follows amongst others from the fact, that the point of contact of each tangent of the C_4 drawn from R must lie on the conic ϱ_2 and must be a coincidence of the involutory (2,2); the number of these tangents amounts thus to four, so that the remaining tangents out of R must coincide two by two in two double tangents.

For further particulars about the properties which can be deduced from these observations I refer to my paper mentioned above and to the paper named in it published in "N. Archief voor Wiskunde, XIV."

4. We shall now suppose that O_1 and O_2 are *biflecnodal points*. Let us choose the point O_3 in such a way, that the tangents in O_1 and in O_2 are separated harmonically by O_1O_2, O_1O_3 resp. by O_2O_1, O_2O_3, then the equation of C_4 has the form

$$x_1^2x_2^2 - a_1^2x_2^2x_3^2 - a_2^2x_1^2x_3^2 + b_0x_1x_2x_3^2 + b_1x_1x_3^3 + b_2x_2x_3^3 + c^2x_3^4 = 0.$$

If O_1 and O_2 are to become biflecnodal points, then we shall every time have to find when substituting $x_1 = \pm a_1x_3$ and $x_2 = \pm a_2x_3$ that $x_3^4 = 0$. For this is necessary $b_2 \pm a_1b_0 = 0$ and $b_1 \pm a_2b_0 = 0$, thus $b_0 = 0$, $b_1 = 0$ and $b_2 = 0$ [2]).

So we have to deal with the equation

$$x_1^2x_2^2 - a_1^2x_2^2x_3^2 - a_2^2x_1^2x_3^2 + c^2x_3^4 = 0.$$

If we write for this

$$(x_1^2 - a_1^2x_3^2)(x_2^2 - a_2^2x_3^2) + (c^2 - a_1^2a_2^2)\,x_3^4 = 0,$$

and if we put moreover

$$c^2 - a_1^2a_2^2 = f^2,$$

it is evident that C_4 can be generated by the projective involutions of rays

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[1]) The six points r_1s_2, s_1r_2, s_1t_2, t_1s_2, t_1r_2, r_1t_2 lie on a conic; for, through r_1r_2, s_1s_2, t_1t_2 passes the line h.

[2]) We find moreover that C_4 cannot have at the same time a flecnodal point and a biflecnodal point.

$$\left.\begin{aligned} x_1^2 - a_1^2 x_3^2 &= \lambda f x_3^2 \\ f x_3^2 &= -\lambda (x_2^2 - a_2^2 x_3^2). \end{aligned}\right\}$$

In this C_4 thus ∞^1 *quadrangles are described having all O_1 and O_2 as diagonal points.*

The vertices of these quadrangles evidently form a *fundamental involution F_4*.

Out of

$$\left.\begin{aligned} x_1^2 &= (\ a_1^2 + \lambda f)\, x_3^2, \\ \lambda x_2^2 &= (\lambda a_2^2 - \ f)\, x_3^2 \end{aligned}\right\}$$

we find for the diagonals of the quadrangle (λ) the equation

$$(\lambda a_2^2 - f)\, x_1^2 = (\lambda a_1^2 + \lambda^2 f)\, x_2^2.$$

So all quadrangles have in O_3 their *third diagonal point.*

At the same time it is evident from this that we can build up the above mentioned F_4 out of pairs of the fundamental F_2 of which each ray through O_3 contains two pairs.

If the two pairs coincide then the ray which bears them is a double tangent.

The pairs on the ray $x_1 = \varrho x_2$ we find out of

$$f\lambda^2 + (a_1^2 - a_2^2 \varrho^2)\, \lambda + f\varrho^2 = 0.$$

Thus for a double tangent we have

$$(a_1^2 - a_2^2 \varrho^2)^2 = 4 f^2 \varrho^2,$$

or

$$a_2^2 \varrho^2 \pm 2 f \varrho - a_1^2 = 0.$$

So O_3 is the point of intersection of four double tangents corresponding to

$$a_2^2 x_1^2 \pm 2 f x_1 x_2 - a_1^2 x_2^2 = 0,$$

or, what comes to the same, to

$$a_2^2 x_1^2 \pm 2 c x_1 x_2 + a_1^2 x_2^2 = 0.$$

The eight points of contact lie on a conic.

For, the polar curve of O_3 degenerates into $x_3 = 0$ and the conic

$$a_2^2 x_1^2 + a_1^2 x_2^2 - 2 c^2 x_3^2 = 0.$$

5. We shall show now that the remaining four double tangents are connected with two *fundamental involutions of pairs* which can be generated by conics.

The curve C_4 can be generated by the projective pencils

$$\left.\begin{aligned} (x_1 - a_1 x_3)(x_2 - a_2 x_3) &= \varrho f x_3^2, \\ \varrho\, (x_1 + a_1 x_3)(x_2 + a_2 x_3) &= - f x_3^2. \end{aligned}\right\}$$

Evidently the two variable points of intersection of conjugate conics lie on the line

$$2\varrho\,(a_1x_2 + a_2x_1) + (\varrho^2 + 1)\,fx_3 = 0,$$

passing through the point H_1 having as coordinates $(a_1, -a_2, 0)$.

Each line

$$a_1x_2 + a_2x_1 + \sigma fx_3 = 0$$

bears two pairs of the fundamental involution which can be generated by each of the two pencils of conics; for we have $\varrho^2 - 2\sigma\varrho + 1 = 0$.

For $\varrho = \pm 1$ these pairs coincide and we find the *double tangents*

$$a_1x_2 + a_2x_1 \pm fx_3 = 0.$$

In a similar way the pencils

$$\left.\begin{aligned}(x_1 - a_1x_3)(x_2 + a_2x_3) &= \varrho fx_3^2,\\ \varrho\,(x_1 + a_1x_3)(x_2 - a_2x_3) &= -fx_3^2\end{aligned}\right\}$$

determine a fundamental involution which is also generated by the rays out of the point H_2 $(a_1, a_2, 0)$, through which at the same time the double tangents

$$a_1x_2 - a_2x_1 \pm fx_3 = 0$$

pass.

The *four double tangents* form a quadrilateral having $O_1O_2O_3$ as diagonal triangle.

6. The polar line of $(a_1, \pm a_2, 0)$ with respect to the conic

$$(x_1 - a_1x_3)(x_2 \pm a_2x_3) = \varrho fx_3^2$$

is represented by

$$a_1x_2 \pm a_2x_1 = 0.$$

From this ensues that the pencils (H_1) and (H_2) determine two involutory (2,2) on these two lines h_1 and h_2. Their branchpoints are generated by the nodal tangents and the tangents which can still be drawn out of O_1 and O_2.

If we write the equation of C_4 in the form

$$(x_1^2 - a_1^2x_3^2)\,x_2^2 - (a_2^2x_1^2 - c^2x_3^2)\,x_3^2 = 0,$$

it is evident that the lines

$$a_2^2x_1^2 = c^2x_3^2$$

touch it on $x_2 = 0$.

In an analogous way the lines

$$a_1^2x_2^2 = c^2x_3^2$$

have their points of contact on $x_1 = 0$.

And now we see directly that these two pairs of rays intersect each other on the lines h_1 and h_2,

$$a_1x_2 \pm a_2x_1 = 0,$$

which bear at the same time the points of intersection of the nodal tangents

$$x_1^2 = a_1^2 x_3^2 \text{ and } x_2^2 = a_2^2 x_3^2.$$

The remaining points of intersection of the two fourrays lie on the conic

$$a_1^2 x_2^2 + a_2^2 x_1^2 - (a_1^2 a_2^2 + c^2)\, x_3^2 = 0.$$

This is immediately evident, if we eliminate out of the equations

$$(a_1^2 x_2^2 - c^2 x_3^2)\,(x_2^2 - a_2^2 x_3^2) = 0,$$
$$(a_2^2 x_1^2 - c^2 x_3^2)\,(x_1^2 - a_1^2 x_3^2) = 0$$

the quantity x_3^4.

The coincidences on h_1 and h_2 here also originate from the tangents out of H_1 and H_2. Indeed we find for the polar curves of H_1 and H_2

$$a_1(x_1 x_2^2 - a_2^2 x_1 x_3^2) \pm a_2(x_1^2 x_2 - a_1^2 x_2 x_3^2) = 0,$$

or

$$(a_1 x_1 \pm a_2 x_2)\,(x_1 x_2 \mp a_1 a_2 x_3^2) = 0.$$

From this is evident at the same time that the conics

$$x_1 x_2 \mp a_1 a_2 x_3^2 = 0$$

generate the points of contact of the double tangents meeting in H_1 and H_2.

By combining the equation

$$x_1^2 x_2^2 - a_1^2 a_2^2 x_3^4 = 0$$

with the equation of C_4 we find that the eight points of contact of the four double tangents are situated on the conic

$$a_2^2 x_1^2 + a_1^2 x_2^2 = (a_1^2 a_2^2 + c^2)\, x_3^2$$

7. The curve of Hesse is represented by

$$(a_1^2 x_2^2 + a_2^2 x_1^2)\, x_1^2 x_2^2 + \{(8a_1^2 a_2^2 - 6c^2)\, x_1^2 x_2^2 - (a_1^2 x_2^2 + a_2^2 x_1^2)^2\}\, x_3^2 +$$
$$+ (a_1^2 a_2^2 - 2c^2)\,(a_1^2 x_2^2 + a_2^2 x_1^2)\, x_3^4 + 2a_1^2 a_2^2\, c^2 x_3^6 = 0.$$

If we eliminate $x_1^2 x_2^2$ out of this equation and the equation of C_4,

$$x_1^2 x_2^2 - (a_1^2 x_2^2 + a_2^2 x_1^2)\, x_3^2 + c^2 x_3^4 = 0,$$

it is evident that the points which the two curves have in common besides O_1 and O_2 are situated on the conic

$$3\,(a_2^2 x_1^2 + a_1^2 x_2^2) = 2c^2 x_3^2.$$

The eight points of inflexion of a C_4 with two biflecnodal points are points of intersection with a conic.

They lie two by two on four right lines through the point of intersection O_3 of the four double tangents of the first group.

The polarcurve η_3 of the point (y) is represented by

$$(y_1 x_2 + y_2 x_1) x_1 x_2 - y_3 (a_1^2 x_2^2 + a_2^2 x_1^2) x_3 - (a_1^2 y_2 x_2 + a^2_2 y_1 x_1) x_3^2 + 2c^2 y_3 x_3^3 = 0.$$

As it is touched in O_1 and O_2 by the lines

$$y_2x_2 - a^2_2y_3x_3 = 0 \quad \text{and} \quad y_1x_1 - a_1^2y_3x_3 = 0,$$

we find that

$$y_1y_2x_1x_2 - a_1^2y_2y_3x_2x_3 - a_2^2y_1y_3x_1x_3 + c^2y_3^2x_3^2 = 0$$

represents a conic η_2 touching the polar curve in O_1 and O_2.

If (y) lies on C_4, then

$$y_1^2y_2^2 - a_1^2y_2^2y_3^2 - a_2^2y_1^2y_3^2 + c^2y_3^4 = 0,$$

i. e. (y) also belongs to η_2. The tangent (y) to η_2 has as equation

$$y_1y_2(y_1x_2+y_2x_1) - (a_1^2y_2^2+a_2^2y_1^2)y_3x_3 - y_3^2(a_1^2y_2x_2+a_2^2y_1x_1) + 2c^2y_3^3x_3 = 0.$$

As when (x) and (y) are exchanged it determines the polar curve η_2 it represents at the same time the tangent in (y) to C_4.

In each of its points C_4 is touched by a conic which touches the polar curve of that point in the biflecnodal points.

The curves C_4 and η_2 have two more points in common. If l is their connecting line, then the pencil determined by C_4 and $\eta_2 + l$ contains a curve composed of η_2 and a second conic. From this ensues: *The points of contact of the six tangents out of a point of* C_4 *can be connected by a conic.*

8. The projective involutions of rays (O_1) and (O_2) have as double rays

$$\left.\begin{array}{ll} \lambda = \infty, & x_3^2 = 0, \\ \lambda = -a_1^2 : f, & x_1^2 = 0. \end{array}\right\} \text{ and } \left\{\begin{array}{ll} \lambda = 0, & x_3^2 = 0, \\ \lambda = f : a^2_2, & x_2^2 = 0. \end{array}\right.$$

When the double rays O_2O_3 and O_1O_3 are conjugated to each other, their point of intersection becomes a third double point of C_4. This takes place when we have

$$\frac{f}{a_2^2} + \frac{a_1^2}{f} = 0, \text{ or } c^2 = 0.$$

The C_4 is then represented by

$$x_1^2x_2^2 - a_1^2x_2^2x_3^2 - a_2^2x_1^2x_3^2 = 0.$$

So it has *three biflecnodal points.* As is evident from the above we can describe in this C_4 ∞ quadrangles having the three double points as diagonal points.

The double tangents of the first group are now replaced by the tangents in O_3 (§ 4). In each of the biflecnodal points the tangents are harmonically separated by the lines to the remaining two double points.

The C_4 with three biflecnodal points have been extensively treated by LAGUERRE (*Nouv. Ann.* 2^e^ série XVII, 1878) and by SCHOUTE (*Archiv der Math. und Phys.* 2^e^ Reihe, II, III, IV, VI, 1885—87).

Mathematics. — *"On curves which can be generated by projective involutions of rays."* By Prof. JAN DE VRIES.

1. By the symbol

$$(a_1x_1 + a_2x_2)^{(n)}$$

we shall indicate a homogeneous form of order n.

By the projective involutions of rays

$$(a_2x_2 + a_3x_3)^{(n)} + \lambda\,(\alpha_2x_2 + \alpha_3x_3)^{(n)} = 0,$$
$$(b_1x_1 + b_3x_3)^{(n)} + \lambda\,(\beta_1x_1 + \beta_3x_3)^{(n)} = 0$$

a curve C_{2n} is generated in which ∞^1 $2n$-sides are described possessing in O_1 and O_2 n-fold vertices. For brevity I call such a $2n$-side *bisingular.*

O_1 and O_2 are n-fold points of the curve. The tangents in O_1 form a group of the first involution which is conjugated to the group of the second containing the ray O_2O_1. These two groups determine a singular $2n$-side, where O_1 replaces $\frac{1}{2}\,n\,(n+1)$, and O_2 replaces $\frac{1}{2}\,n\,(n-1)$ vertices.

If we can describe in a C_{2n} with two n-fold points one bisingular $2n$-side it bears an infinite number of those figures.

For, if the indicated $2n$-side is represented by the two groups of rays

$$(a_2x_2 + a_3x_3)^{(n)} = 0 \quad , \quad (b_1x_1 + b_3x_3)^{(n)} = 0\,,$$

and if $x_3 = mx_2$ is one of the rays of the first group, then the substitution must furnish $x_2{}^n\,(b_1x_1 + b_3mx_2)^{(n)} = 0$, $x_3 = mx_2$, O_1 being an n-fold point. Hence the equation of C_{2n} must have the form

$$(a_2x_2 + a_3x_3)^{(n)}\,(\beta_1x_1 + \beta_3x_3)^{(n)} = (b_1x_1 + b_3x_3)^{(n)}\,(\alpha_2x_2 + \alpha_3x_3)^{(n)}\,. \quad (1)$$

But then the equation can be formed by elimination out of

$$\left.\begin{aligned}(a_2x_2 + a_3x_3)^{(n)} + \lambda\,(\alpha_2x_2 + \alpha_3x_3)^{(n)} = 0,\\ (b_1x_1 + b_3x_3)^{(n)} + \lambda\,(\beta_1x_1 + \beta_3x_3)^{(n)} = 0,\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (2)$$

and the curve contains the ∞^1 bisingular $2n$-sides which can be indicated by these two equations, λ varying.

2. We shall now investigate under which condition two projective involutions of rays will generate a curve C_{2n} with three n-fold points O_k, so that n^2 points of intersection of two conjugate groups of rays are vertices of three different bisingular $2n$-sides having each two of the points O_k as n-fold vertices.

In that case we must be able to bring through the points of intersection of

$$(a_2x_2 + a_3x_3)^{(n)} = 0 \quad \text{and} \quad (b_1x_1 + b_3x_3)^{(n)} = 0$$

a group of rays

$$(c_1x_1 + c_2x_2)^{(n)} = 0$$

It is now at once evident that this is only possible when the first two equations have the following form

$$a_2^n x_2^n - a_3^n x_3^n = 0, \quad a_1^n x_1^n - a_3^n x_3^n = 0,$$

so that we have

$$a_1^n x_1^n - a_2^n x_2^n = 0.$$

Out of

$$a_2^n x_3^n - a_3^n x_3^n + \lambda\,(\alpha_2^n x_2^n - \alpha_3^n x_3^n) = 0$$

and

$$a_1^n x_1^n - a_3^r x_3^n + \lambda\,(\alpha_1^n x_1^n - \alpha_3^n x_3^n) = 0$$

follows

$$(a_2^n x_2^n - a_3^n x_3^n)\ (\alpha_1^n x_1^n - \alpha_3^n x_3^n) - (a_1^n x_1^n - a_3^n x_3^n)\ (\alpha_2^n x_2^n - \alpha_3^n x_3^n) = 0$$

or in transparent notation

$$(a\alpha)_3 x_1^n x_2^n + (a\alpha)_1 x_2^n x_3^n + (a\alpha)_2 x_3^n x_1^n = 0. \quad . \quad . \quad . \quad (3)$$

The tangents in O_3 are represented by

$$(a\alpha)_1 x_2^n + (a\alpha)_2 x_1^n = 0.$$

If $x_2 = kx_1$ is the equation of one of these tangents, then the substitution in the equation of the C_2, evidently furnishes $x_1^{2n} = 0$. In each of the n-fold points each tangent has thus $(n+1)$ points in common with the corresponding branch.

For each value of λ we find a figure consisting of $3n$ lines (of which however only 3 or 6 are real, according to n being even or odd) and $(n^2 + 3)$ points (of which 4 or 7 are real). 1)

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1) We have in particular for $n = 3$ a configuration $(12_3, 9_4)$. From this ensues, by the way, that of the configuration $(9_4, 12_3)$ corresponding dually to it only 3 points and 4 lines can be real. From the above it is evident that the 12 lines of the $(9_4, 12_3)$ can be represented by

$$\left.\begin{array}{l} \xi_1 = 0, \ \xi_2 = 0 \\ \xi_2 = 0, \ \xi_3 = 0 \\ \xi_3 = 0, \ \xi_1 = 0 \end{array}\right\} \text{and } \xi_1 = \varepsilon^k \xi_2 = \varepsilon^l \xi_3, \text{ where } \varepsilon^3 = 1 \text{ is.}$$

The three lines $\xi_3 = \xi_2 = \xi_1$, $\xi_3 = \varepsilon\xi_2 = \varepsilon^2\xi_1$, $\xi_2 = \varepsilon^2\xi_1 = \varepsilon\xi_3$ contain together the 9 points. They are also indicated by

$$x_1 + x_2 + x_3 = 0, \ x_1 + \varepsilon x_2 + \varepsilon^2 x_3 = 0, \ x_1 + \varepsilon^2 x_2 + \varepsilon x_3 = 0.$$

The 9 points lying also on $x_1 x_2 x_3 = 0$, they are the base-points of the pencil

$$(x_1 + x_2 + x_3)\ (x_1 + \ x_2 + \varepsilon^2 x_3)\ (x_1 + \varepsilon^2 x_2 + \varepsilon x_3) + m\, x_1 x_2 x_3 = 0.$$

And so here we have found back the canonical equation of C_3.

3. The projective involutions of rays

$$\left.\begin{aligned}(a_2x_2 + a_3x_3)^{(n)} + \lambda x_3{}^k(\alpha_2x_2 + \alpha_3x_3)^{(n-k)} = 0,\\(b_1x_1 + b_3x_3)^{(n)} + \lambda x_3{}^k(\beta_1x_1 + \beta_3x_3)^{(n-k)} = 0,\end{aligned}\right\} \quad . \quad . \quad . \quad (4)$$

generate evidently a C_{2n-k}, which has O_1 and O_2 as $(n-k)$-fold points and as equation

$$(a_2x_2 + a_3x_3)^{(n)}(\beta_1x_1 + \beta_3x_3)^{(n-k)} = (b_1x_1 + b_3x_3)^{(n)}(\alpha_2x_2 + \alpha_3x_3)^{(n-k)} \quad . \; (5)$$

The two multiple points are for $k > 1$ of a particular kind. For the tangents in O_1 are represented by $(\alpha_2x_2 + \alpha_3x_3)^{(n-k)} = 0$, and each of them has as is evident from substitution $(k+1)$ points in common with the corresponding branch of the curve.

For $x_3 = 0$ we find

$$x_2{}^{n-k}\,x_2{}^{n-k}\,(a_0\beta_0x_2{}^k - b_0\alpha_0x_1{}^k) = 0.$$

Therefore the curve is intersected by O_1O_2 in a group of the involution I_k which has O_1 and O_2 as k-fold points.

If we can describe in a C_{2n-k} with two $(n-k)$-fold points *a bisingular 2n-side* having those multiple points as n-fold points it has an equation of form (5). But then it can be generated by two involutions of form (4) and it bears therefore ∞ *bisingular 2n-sides.*

4. For $k = n$ we find a C_n which will in general not possess any singular points. Yet it is in general not possible to generate a C_n by two involutions of rays of order n. For, the centres O_1 and O_2 of the involutions must be n-fold points of an involution I_n, of which the points of intersection of C_n with O_1O_2 form a group. But then the polar curve of O_1 would have to have $(n-1)$ points in O_2 in common with the right line O_1O_2, and this is not possible for a general C_n.

But each *cubic curve* can be generated by two projective cubic involutions of rays. Their centres O_1 and O_2 are conjugate points of the curve of Hesse, for the two double rays which O_1 possesses (besides the threefold ray O_1O_2), bearing each of them the points of contact of three tangents out of O_2, form the polar conic of O_2, whilst the rays which complete the two double rays to groups of the involution form the satellite conic of O_2.

Let us now take inversely O_1 and O_2 as two conjugate points of the curve of Hesse. We regard O_2 as centre of a cubic involution which has O_2O_1 as threefold element, whilst a second group is formed by three tangents the points of contact of which lie in a line r, so that their points of intersection with C_3 are situated on a line s. The line r counted double and the line s we unite to a group of a cubic involution (O_1) having $O_1 O_2$ as threefold ray. We now make the two involutions projective in such a way that the threefold rays correspond, that the group (rrs) is conjugated to the group of the three tangents and that finally the groups are assigned to each other which are determined by the rays to an arbitrary point of C_3. The two involutions then generate a C_3 having with the given C_3 ten points in common, thus coinciding with it.

In each general cubic curve we can thus describe ∞^2 *bisingular hexagons.*

Their threefold points lie on the curve of **Hesse**.

5. If the ray $O_1 O_2$ counted double belongs to corresponding groups of the cubic involutions (O_1) and (O_2), these involutions generate a C_4 which has O_1 and O_2 as points of inflection the tangents of which meet each other on the curve. For, out of

$$a_0 x_2^3 + 3a_1 x_2^2 x_3 + 3a_2 x_2 x_3^2 + a_3 x_3^3 + \lambda x_2 x_3^2 = 0,$$
$$b_0 x_1^3 + 3b_1 x_1^2 x_3 + 3b_2 x_1 x_3^2 + b_3 x_3^3 + \lambda x_1 x_3^2 = 0$$

we find

$$(a_0 x_2^3 + 3a_1 x_2^2 x_3 + 3a_2 x_2 x_3^2 + a_3 x_3^3) x_1 = (b_0 x_1^3 + 3b_1 x_1^2 x_3 + 3b_2 x_1 x_3^2 + b_3 x_3^3) x_2,$$

and this is satisfied by

$$x_1 = 0,\ x_2 x_3^3 = 0 \text{ and } x_2 = 0,\ x_1 x_3^3 = 0.$$

According to the rule found in § 3 $O_1 O_2$ is harmonically divided by C_4.

Inversely, *when two stationary tangents of a* C_4 *intersect each other on the curve whilst their points of contact are harmonically separated by* C_4, *then those points are threefold vertices of* ∞^1 *bisingular hexagons described in* C_4.

For, in that case the equation of C_4 has the form

$$(c_1 x_1^2 + c_2 x_2^2) x_1 x_2 + (f_1 x_1 + f_2 x_2 + f_3 x_3)\, x_1 x_2 x_3 + (g_1 x_1 + g_2 x_2) x_3^3 = 0.$$

If we replace it by

$$\{c_1 x_1^3 + f_1 x_1^2 x_3 + (\tfrac{1}{2} f_3 + \varrho) x_1 x_3^2 + g_2 x_3^3\} x_2 +$$
$$\{c_2 x_2^3 + f_2 x_2^2 x_3 + (\tfrac{1}{2} f_3 - \varrho) x_2 x_3^2 + g_1 x_3^3\}\, x_1 = 0,$$

it is evident, that the curve can be generated by the pencils

$$\left.\begin{array}{l} c_1 x_1^3 + f_1 x_1^2 x_3 + (\tfrac{1}{2} f_3 + \varrho)\, x_1 x_3^2 + g_2 x_3^3 + \lambda x_1 x_3^2 = 0, \\ c_2 x_2^3 + f_2 x_2^2 x_3 + (\tfrac{1}{2} f_3 - \varrho)\, x_2 x_3^2 + g_1 x_3^3 - \lambda x_2 x_3^2 = 0. \end{array}\right\}$$

Here we can still replace $(\lambda + \varrho)$ by μ.

Physics. — "*On the law of the partition of energy in electrical systems.*" By Prof. J. D. VAN DER WAALS JR., (Communicated by Prof. J. D. VAN DER WAALS).

It is well known that MAXWELL was the first to pronounce the thesis that in the case of statistical equilibrium every degree of freedom will possess on an average the same amount of kinetic energy. In my opinion BOLTZMANN's and GIBBS's investigations have raised the validity of this thesis for the systems to which their theory applies, above doubt. And yet this result is difficult to reconcile with the experimental data. It has already long been known that the gas molecules must undoubtedly possess more degrees of freedom than would follow from the specific heat at constant volume in connection with this law.

BOLTZMANN [1]), GIBBS [2]) and others have expressly stated that systems, as they occur in nature, always exhibit important points of difference with the systems for which the said law was proved. For BOLTZMANN and GIBBS have drawn up their statistical theory exclusively for systems which have a finite number of degrees of freedom, and for which the equations of classical mechanics hold. The systems occurring in nature, on the other hand, always contain electrical charges; so we have always to deal with the ether with its infinite number of degrees of freedom. Moreover for the changes of the coordinates no longer the mechanical laws are exclusively to be taken into consideration, but also the fundamental equations of the theory of electricity.

In view of this an extension of the statistical method, in such a way that it applied also to electrical phenomena, was urgently required. An attempt at such an extension was made by JEANS [3]) and by LORENTZ [4]). They arrived both at the conclusion that also in this case the law of equal partition of energy holds. Their considerations, however, pointed out a new difficulty. When every degree of freedom possesses the same amount of kinetic energy, the ether with its infinite number of degrees of freedom would finally acquire all the energy. A consequence of this would be that in case of equilibrium between a material system and the ether, as is found in all heat phenomena in consequence of the radiation, the velocities of the molecules and the electrons would become zero. Moreover the ether would then have to contain the energy in such a way that all the energy had accumulated on the side of the infinitely small wave-lengths.

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[1]) L. BOLTZMANN, Wiener Sitzungsb. LXIII p. 418. a. 1871.

[2]) J. W. GIBBS, Statistical Mechanics. p. 167.

[3]) J. H. JEANS, Phil. Mag. Series VI. Vol. X, p. 91, 1905.

[4]) H. A. LORENTZ, Nuovo Cimento, Series V. Vol. XVI.

It is clear that here too theory is in direct contradiction with experience. Still it is easy to see that we must come to this conclusion if we assume the three following suppositions:

A. The relation $\sum_{r=1}^{r=n} \frac{d\dot{p}_r}{dp_r} = 0$ is satisfied. Here n represents the total number of independent variables, p_r an arbitrary of these variables. In mechanics both the generalized coordinates and their time variations or the corresponding momenta are to be considered as independent, so that in a mechanic system n represents twice the number of degrees of freedom.

B. There is statistical equilibrium.

C. All the phases (in the sense of GIBBS) representing the same energy, lie on the same path.

By JEANS[1]) and by W. RITZ[2]) attempts have been made to explain this contradiction between theory and observation. In a certain sense also by M. PLANCK, though the latter does not start from GIBBS's statistical method in his theory of radiation. As none of these theories satisfies me entirely, I shall state here another direction in which a solution of the contradiction might be sought. Before proceeding to this, however, I consider it my duty to indicate why the three theories mentioned do not satisfy me, as else I should not be justified in adding another view to the number of existing ones.

On a superficial consideration RITZ's theory makes the impression to look for the solution of the difficulty in this that it rejects supposition *C.* For RITZ wants to reject a great number of states of the electromagnetic field which are compatible with the field equations, because in his opinion they cannot occur. Thus he assumes only waves originating from electrons, not such ones as converge on them, because, if the latter existed, the electron would be a perpetuum mobile. From these words it appears already that it is really supposition *B* that is rejected by RITZ. The system he considers, constantly loses energy, and so it is not in equilibrium. If we think the material universe to occupy a finite space surrounded by an ether which reaches to infinity, it must of course lose energy, and cannot be in equilibrium. But then we knew already that on account of the prevailing differences of temperature the material universe is not in equilibrium. We have always only to deal with limited systems which are surrounded by other systems, and which are only for a certain limited time excluded from external influence, and may be considered to be in equilibrium. During the time, however, that the equilibrium exists, every particle must on an average absorb as much energy as it emits. So an inward radiant vector must exist during that time.

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[1]) Comp. i. a. l.c. and Phil. mag. Series VI. Vol. II, p. 638.

[2]) RITZ. Phys. Zeitschr. Vol. IX. No. 25 p. 907. Anno 1908.

But, says Ritz, when we consider a finite system, we must always think it enclosed within walls which contain a finite number of electrons, and which therefore can reflect the radiation in fewer ways than Lorentz's totally reflecting walls can. So Lorentz's theory is not applicable to the natural systems. This really offers a difficulty. Even the γ-rays of radium pass through metal screens in a considerable degree, and it is possible that vibrations of still smaller wave-length possess so great a penetrating power that they are never in equilibrium of radiation in our experiments. Yet it seems to me that there are facts which indicate that in Ritz's observation, which is quite correct in itself, the clue to the explanation of the normal spectrum is not to be found. For it seems to me that if Ritz's explanation was the true one, the spectral formula of Rayleigh would have to hold for all wave-lengths which are still regularly reflected by the walls, which is by no means the case. Moreover, we should then have to expect that this formula would be fulfilled with the greater degree of approximation as the walls were thicker, and so more wave-lengths were approximately in equilibrium of radiation; then we should not find a definite spectral formula independent of the thickness of the walls. We may finally imagine the walls to be infinitely thick, so that they would contain an infinite number of electrons, and Ritz has not shown that also in this case his restriction of the number of possibilities in the inward radiation originating from the walls, is justified.

While Ritz's theory deals only with the normal spectrum, Jeans tries at the same time to find a solution of the difficulties attached to it, and of the difficulties attached to the specific heats. He, too, thinks that he has to find the solution in the fact that supposition B is not satisfied. He thinks, namely, that the coordinates of a system may be divided into two kinds: 1 those which we may call conservative coordinates, which possess an appreciable kinetic energy; 2 those which we may call dissipative coordinates, which can receive energy from the conservative ones only exceedingly slowly, and which lose the energy they have received so rapidly by radiation, that they never possess an appreciable quantity of energy. Then the kinetic energy which must be ascribed to systems agrees with their number of conservative coordinates and so is less than would correspond with the total number of degrees of freedom. So this agrees with what we observe with regard to specific heat.

An objection to this theory is, that it is inexplicable how such a system could be heated by radiation. For then the dissipative coordinates would first absorb heat, and then transfer it to the conservative coordinates. But they can only transfer it, when on an average they have more kinetic energy than the conservative coordinates. So if such a body was exposed to the radiation of a hotter body, it would absorb very much heat before the temperature began to rise, and on further heating by radiation the dissipative coordinates, too, would have to receive energy, and the specific heat would therefore be greater than when the heating was done by conduction. On account of these and similar conclusions which might be made from JEANS's theory, this theory did not seem satisfactory.

Finally in PLANCK's theory it is not possible to ascertain which of the three suppositions is to be rejected. Still it is clear that we can never obtain PLANCK's spectral formula, if we accept the three suppositions. His suppositions must, therefore, be incompatible with the three suppositions given here, and probably the hypothesis that the energy can only be absorbed in fixed energy-quanta, will be irreconcilable with our suppositions. Of course, this is no objection to PLANCK's theory; the assumption of the three suppositions bringing us into conflict with experience, one of them must in reality not be fulfilled. Of more importance seems to me the objection that the supposition of these fixed quanta of energy which can only be absorbed or radiated as a whole, and which, moreover, have a different amount for radiation of different wave-length, clash altogether with all our ideas on the behaviour of vibrators, and that it is difficult to see how it could be reconciled to the ordinary laws of radiation by vibrators, of which PLANCK also made use in his theory.

Nor would this objection perhaps suffice to make us reject the theory, when there were urgent reasons why we should have to assume the existence of these energy-quanta. In my opinion, however, these urgent reasons are wanting. PLANCK used the supposition of the existence of these energy-quanta to bring two equations into harmony, which have been derived in an entirely different way. One[1]) has been derived from the laws of BOLTZMANN (STEPHAN) and WIEN, which are again derived from the 2nd law of thermodynamics in connection with the fundamental equations of the theory of electricity, and which, therefore, hold for all the systems for which these laws hold.

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[1]) M. PLANCK. Vorlesungen über die Theorie der Wärmestrahlung p. 149 equation 223.

This equation runs $S = F\left(\frac{u}{\nu}\right)$, in which S represents the entropy, u the energy, ν the frequency of the free vibrations of the vibrator and F a still unknown function. The other equation[1]) may be written $S = F\left(\frac{u}{\varepsilon}\right)$ in which ε represents a small quantum of energy, into which the total energy of all vibrators with frequency ν is divided, after which these atoms of energy are distributed over the different vibrators according to the laws of probability. If these equations are to be in harmony, ε must really be $= h\nu$, as Planck assumes. The question, however, is, whether there is sufficient cause to assume that these equations do harmonise. And in my opinion this is not the case. For the first equation holds for real bodies, the second for the fictitious systems of vibrators, which most likely do not occur in the real bodies. In the first place so many different kinds of vibrators with so many different free periods are hardly to be assumed. And moreover every vibrator will, no doubt contain a moving electron whose motion strictly speaking is controlled not by a differential, but by an integral equation, so that the vibrator has not one, but a whole series of periods for its free vibrations.

Now Planck asserts that it is of no importance whether his radiating systems agree with those really occurring in nature. For, he says[2]), Kirchhoff's law teaches that we always get the same normal spectrum independent of the nature of the walls. This, however, seems to me an inaccurate interpretation of the law of Kirchhoff. For this law states only something about walls occurring in nature, but it does not decide anything about the spectrum that would be formed in a space inclosed by walls with fictitious properties which deviate from what really occurs in nature. Hence the interpretation of Kirchhoff's law that the spectrum would be independent of the nature of the walls, is to be rejected. The real gist of the law is much better rendered by saying that all walls occurring in nature have such properties that they give rise to the same spectrum; what these properties are which all real walls have in common, is not yet quite known. Only on special suppositions did Lorentz[3]) succeed in examining this.

That this acceptation of Kirchhoff's law is really the correct one appears from this that in his cited paper Lorentz succeeded in imagining walls of such a nature that the thermodynamic laws of radiation are not fulfilled in their mutual radiation. He imagined, viz., two uniform systems, of which the linear measures of the second are α-times larger, all masses β-times larger, and all charges of corresponding parts β/α-times larger than of the first. It now appeared that when the velocities of the parts of the systems were the same, that then the ratio of the electrical forces in corresponding points was $\sqrt{\beta/\alpha^3}$, so the ratio of the densities of energy β/α^3. Then, however, the ratio of the temperatures is as that of the kinetic energy of corresponding particles, i. e. $\beta : 1$, so that the law of BOLTZMANN is fulfilled only when $\beta^4 = \beta/\alpha^3$ or $\beta = 1/\alpha$. As, however, it is always possible to imagine these systems in such a way that α is not $1/\beta$, it appears that the thermodynamic laws of radiation are not fulfilled for arbitrarily chosen systems. So when we make arbitrary suppositions concerning the nature of the walls, we run a great risk of choosing them in such a way that the spectral distribution with which they would be in equilibrium, does not agree with the real normal spectrum, this could only be incidentally the case. And so there is no ground to assume that the two formulae of PLANCK mentioned represent the same spectrum, which removes the ground for the assumption of the energy-quanta.

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[1]) loc. cit. p. 153 in the middle.

[2]) loc. cit. p. 100 and 101.

[3]) H. A. Lorentz, These Proc. IX p. 436, 1900.

JEANS [1]) considers it a difficulty to assume that walls could be imagined for which the thermodynamic laws of radiation are not fulfilled. I do not see the difficulty. The thermodynamic laws are only empiric laws. And when we come to the conclusion that the radiation of arbitrarily imagined walls does not satisfy the second law of thermodynamics, whereas experience teaches that the real radiation does satisfy it, we have simply to conclude from this that such walls do not occur in nature. We should, indeed, meet with a difficulty, if we could show that the laws of thermodynamics *had to* be applicable to all conceivable systems. The statistical derivation of these laws seems really to imply this. This, however, is only seemingly the case. For any fictitious system, whatever properties we ascribe to it, a state of statistical equilibrium will, no doubt, exist which is characterized by the fact that a certain quantity, which we may call the probability, is maximum. If we call the logarithm of the probability entropy, then for every system the theorem will hold that with given energy and volume this entropy is maximum. But it has not been proved a priori that the entropy defined in this way, is always represented by $\int \frac{dQ}{T}$, or at least it has only been proved for mechanical systems, and not for electrical ones, which we are now discussing. It is not even self-evident by any means that a temperature could be defined for every conceivable system. And we even know that two walls of the nature LORENTZ has loc. cit. imagined, when their particles had the same kinetic energy, so that they were in equilibrium of temperature as regards their conduction of heat, would transfer heat to each other by radiation. And reversely, they would not be in equilibrium of conduction of heat when they were in equilibrium for the radiation. As now in the derivation of the law of STEPHAN with the aid of the cycle of operations described by BARTOLI and BOLTZMANN use is made of the supposition that $\eta = \int \frac{dQ}{T}$, this law need not hold for an arbitrarily imagined body, and can only do so incidentally.

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[1]) J. H. JEANS, Phil. Mag. Series VI Vol. XII p. 57, 1906.

In virtue of the above I think that other explanations are called for, which might be able to reconcile theory and observation. And it seems to me that such an explanation might be found in this direction that we assume that the supposition A is not fulfilled, and this we may do without introducing new hypotheses, without coming in conflict with the current theory of electricity. It is true that JEANS and LORENTZ have come to the conclusion that supposition A *is* satisfied, but it seems to me that their considerations only refer to electrons which possess a mechanical mass; they do not seem to apply to electrons without mechanical mass.

To show this we shall consider systems agreeing with those examined by LORENTZ [1]). A number of electrons are enclosed in a parallelopiped space with totally reflecting walls. It is true that the objection advanced by RITZ to such walls, is not to be entirely refuted, but without this supposition we can never imagine a system in statistical equilibrium, and when we think the space so large that the radiation reflected by the walls, has long been absorbed before it has reached the central parts, the condition in the central parts will most likely not be influenced by the walls. Besides, the reflected radiation will behave in almost the same way as if it was emitted by a medium of the same nature outside the enclosed space, so that also the parts lying nearer the walls will probably be in the same condition as if the walls did not exist, and the medium extended also outside the walls.

I shall assume the electrons to be spherical, so that their position is entirely determined by the cartesian coordinates XYZ of the centre. As further data I shall choose the electrical and the magnetical forces in the different elements of space. In their stead we might also have chosen the coordinates used by LORENTZ; this would have been more symmetrical and more elegant. The coordinates chosen by me however, may allow us to determine the quantities, which we wanted to determine, in a somewhat simpler manner. For the rest the result of the investigation is the same in the two cases.

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[1]) H. A. LORENTZ, Nuovo Cimento l. c.

It is, however, clear that we may not choose the three components of the electrical force $\mathfrak{E}$ and the magnetic force $\mathfrak{H}$ quite arbitrarily in every point. For $\mathfrak{H}$ must satisfy the equation Div. $\mathfrak{H} = 0$, and Div. $\mathfrak{E}$ is also determined in every point if X, Y, and Z are given for every electron. So if we take $\mathfrak{E}_x$, $\mathfrak{E}_y$, $\mathfrak{H}_x$ and $\mathfrak{H}_y$ as independent variables, $\mathfrak{E}_z$ and $\mathfrak{H}_z$ are determined, with the exception of the constant of integration. This constant, however, is not arbitrary, but determined by the conditions that the normal component of $\mathfrak{H}$ and the tangential one of $\mathfrak{E}$ must be zero at the walls. These conditions yield more equations than the number of constants at our disposal. Hence we have still to diminish the number of independent variables by considering still fewer components as independent variables in the elements adjoining the wall. However, I do not think this will affect our further reasoning.

Of course the conditions $Div\, \mathfrak{E} = \varrho$ and $Div\, \mathfrak{H} = 0$ cannot be rigorously satisfied, when we really think $\mathfrak{E}$ and $\mathfrak{H}$ constant within the elements. We can then take it e. g. in such a way that we understand the mean values in the elements by the given components of $\mathfrak{E}$ and $\mathfrak{H}$, while inside these elements $\mathfrak{E}$ and $\mathfrak{H}$ are linear functions of x, y and z, and they do not show any discontinuities on the boundaries of the elements.

The changes of state in our systems are now determined by the following equations:

$$c\, Rot\, \mathfrak{E} = -\frac{d\mathfrak{H}}{dt} \qquad c\, Rot\, \mathfrak{H} = \frac{d\mathfrak{E}}{dt} + \varrho\mathfrak{v}$$

$$\int \varrho\, (\mathfrak{E} + [\mathfrak{v}\, \mathfrak{H}])\, dv = m\dot{\mathfrak{v}}_0$$

$$\int \varrho\, [\mathfrak{r}\, (\mathfrak{E} + [\mathfrak{v}\, \mathfrak{H}])]\, dv = M\dot{\mathfrak{w}}.$$

In these latter two vector formulae, which yield six scalar equations when written down for the different components, $\mathfrak{r}$ represents the radius vector from the centre of the electron to an arbitrary point, m the mass, M the moment of inertia, and $\mathfrak{v}$ the velocity of an arbitrary point, so that $\mathfrak{v} = \mathfrak{v}_0 - [\mathfrak{r}\, \mathfrak{w}]$, when $\mathfrak{r}_0$ denotes the velocity. If this value of $\mathfrak{v}$ is substituted, six equations are obtained in which the six components of $\mathfrak{v}_0$ and $\mathfrak{w}$ occur linearly.

We have here at once to distinguish two cases:

1. m and M are not zero, i. e. we assign a real mass to the

electrons. In this case the equations serve to determine the accelerations, the velocities are to be considered in this case as independent variables.

2. For some electrons m and M are zero. In this case the accelerations disappear from the equations. Now we can solve the components of $\mathfrak{v}_0$ and $\mathfrak{w}$ in determinant form, as they form a set of six linear equations. The elements of this determinant are integrals which are to be extended over the electron, and are known if $\mathfrak{E}$ and $\mathfrak{H}$ have been given in every point. So $\mathfrak{v}_0$ and $\mathfrak{w}$ appear not to be independent variables in this case. The number of variables is, therefore, smaller than in the case that the masses are not zero. And this is not strange: in the expression of the kinetic energy the velocities of the electron do not occur when we ascribe the energy to the medium. Only if by the supposition of a quasi-stationary motion a connection is established between the motion of the electron and the forces of the field, the equation of the energy can be reduced to such a form that $\mathfrak{v}_0$ and $\mathfrak{w}$ occur in it.

The values of $\mathfrak{v}_0$ and $\mathfrak{w}$ thus found must now be substituted in the equation $c\, Rot\, \mathfrak{H} = \frac{d\mathfrak{E}}{dt} + \varrho \mathfrak{v}$ to find the value of $\frac{d\mathfrak{E}}{dt}$.

If we now examine in how far supposition A has been fulfilled, it is at once evident that this is certainly the fact in the first case. Then $\frac{\partial \dot{p}}{\partial p} = 0$ even for every variable separately.

In the second case, however, it is different, then $\frac{\partial \mathfrak{v}_{0x}}{\partial X}$ is not zero. For the integrations occurring in the elements of the determinant which determines $\mathfrak{v}_0$, must be extended over another region when the electron is displaced. When differentiating we should bear in mind that $\mathfrak{E}_z$ is determined from ϱ, whereas ϱ changes in the points of the space if the electron is displaced, so that $\mathfrak{E}_z$ is to be considered as function of X, Y, Z.

It follows from $\frac{d\mathfrak{H}}{dt} = -Rot\, \mathfrak{E}$ that $\frac{d\mathfrak{H}}{dt}$ is independent of $\mathfrak{H}$, so that the terms $\frac{\partial \frac{d\mathfrak{H}}{dt}}{\partial \mathfrak{H}}$ are zero. The same holds for the terms $\frac{\partial \frac{d\mathfrak{E}_x}{dt}}{\partial \mathfrak{E}_x}$ for elements which fall outside the electrons; but not for terms inside them. For there $\frac{d\mathfrak{E}_x}{dt}$ is determined by $\frac{d\mathfrak{E}_x}{dt} = Rot_x\, \mathfrak{H} - \varrho \mathfrak{v}_x$ and $\mathfrak{v}_x$ being dependent on $\mathfrak{E}_x$, this is also the case for $\frac{d\mathfrak{E}_x}{dt}$. It is true that

$\frac{\partial \frac{d\mathfrak{E}_x}{dt}}{\partial \mathfrak{E}_x}$ becomes very small for every element, and zero in the limiting case that we take infinitesimal volume-elements, but the sum of these quantities for all the elements falling within a certain electron does not become zero, but when the volume-elements become infinitely small it verges to a certain limit, which is not to be neglected by the side of $\frac{\partial \mathfrak{r}_{0x}}{\partial X}$. Here too, we must remember that we must not only differentiate with respect to $\mathfrak{E}_x$ where this quantity occurs explicitly, but also that $\mathfrak{E}_z$ depends on $\mathfrak{E}_x$. For by varying $\mathfrak{E}_x$, we vary ϱ, unless we take care to bring about a suitable modification in $\mathfrak{E}_z$ in the surrounding elements.

Equation $\frac{1}{D}\frac{dD}{dt} = -\sum_{r=1}^{r=n} \frac{\partial \dot{p}_r}{\partial p_r}$ now indicates that we have a stationary state if on every path covered by a system the density of phase is made to satisfy $D = e^{-\frac{1}{\vartheta}\int \Sigma \frac{\partial \dot{p}}{\partial p} dt}$. On account of the intricate form which $\Sigma \frac{\partial \dot{p}}{\partial p}$ assumes it seems hardly possible to draw further conclusions, unless we succeed by a felicitous reduction or by making a better choice of the independent variables from the beginning in rendering this sum in a much simpler form.

For the present I must confine myself to pointing out that it seems that in this direction a solution is to be found of the contradiction which has existed up to now between theory and observation. And if this should prove to be the only way in which this can be done, it is a qualitative proof of the existence of electrons without mechanical mass.

We must, however, point out that it can only prove that some electrons do not possess any mechanical mass, not that this would have to be the case for all electrons. For as soon as electrons without mechanical mass occur, the relation $\Sigma \frac{\partial \dot{p}}{\partial p} = 0$ is not fulfilled. The supposition that some, e. g. the positive electrons will possess mechanical mass, and others e. g. the negative electrons not, is by no means excluded by these considerations.

If we should take Kirchhoff's law as holding for arbitrarily imaginable walls, the partition of the energy in the normal spectrum would of course never enable us to conclude anything concerning the nature of the bodies by which the radiation is emitted. If, however, this view is the correct one that the bodies give the same spectrum only because they have certain properties in common, then it must be possible to learn something about these properties from the partition of energy in the spectrum. And thus we may hope that a further development of the application of the statistical method to electrical systems may tend — not to find an accurate formula for the spectrum, which would only be possible if we a priori perfectly knew the nature of the electrons — but rather to test whether a hypothesis concerning the nature of the electrons gives rise to the correct spectral formula, and so whether it is to be accepted or rejected.

Botany. — "*Some remarks on Sciaphila nana Bl.*" By Prof. F. A. F. C. Went.

While working at the *Triuridaceae,* collected by Mr. G. M. Versteeg during the expedition to Southern New-Guinea in 1907, I have also examined the plants of the same order, which are found in the Botanical Museum of the University of Utrecht. In so doing I came across alcoholic material of a *Sciaphila* brought from Buitenzorg by Mr. Pulle and collected at Tjiomas.

When an attempt was made to name this plant, it at once became evident, that it was not *Sciaphila tenella* Bl. and it was therefore surmised that the other species described for Java, namely, *S. nana* Bl., had been met with. Now the diagnosis of Blume is of such a nature, that it is impossible with its aid to recognize the species[1]); nor are the figures of his plate XLVIII conspicuously clear. I soon found, by comparison with Beccari's monograph of Malay *Triuridaceae,* that the specimen in question evidently agreed completely with his *S. corniculata*[2]). I will shortly give detailed proof of this identity, but first remark that Beccari himself had noticed the agreement between Blume's *S. nana* and his own *S. corniculata*, for he speaks of *S. nana*[3]) as follows:

"Non ho visto questa Specie, ma dalla figura lasciata da Blume mi sembra poterla includere nel gruppo della *S. corniculata* e della *S. Arfakiana*".

In order to obtain greater certainty I have examined the original specimen of Blume's in 's Rijks Herbarium at Leiden.

Under the name of *Sciaphila nana* Bl. there are here found, pasted on one sheet of paper, three plants, numbered 1, 2 and 3. Reichenbach had written there: Mihi specimina 2—3 sint tenella, specimen 1 nana Bl. tantum H.G. Rb. fil." I completely share this opinion; there can be no doubt, that 2 and 3 are specimens of *S. tenella* Bl., while the other specimen is the one, which served for Blume's diagnosis, as it is exactly the same as that used for the illustration of the habit. Only in this illustration two flowers are still present, whereas the specimen now possesses but a single one. This renders the Leiden herbarium specimen of little use for determination, as one would at most be justified in sacrificing a part of it, when preparing a monograph of the order, supposing also that one had sufficient reason for assuming, that no new species of *Sciaphila* will be discovered, a by all means remote contingency.

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[1]) C. L. Blume. Museum Botanicum Lugduno-Batavum I. p. 322. 1849—1851.

[2]) O. Beccari. Malesia III. p. 336. Tav. XXXIX. Fig. 5—13. 1886—1890.

[3]) O. Beccari. l. c. p. 338.

As was mentioned, the specimen of the Utrecht museum is certainly identical with Beccari's *S. corniculata*. I will now mention the reasons for this conclusion. Since staminodes are wanting in the female flowers, and the rudiments of pistils in the male flowers (which have three stamens), and since the style is found on the top of the ovary, it is clear that our plant belongs to the subgenus *Hyalisma*. Here several species are further excluded, because in the centre between the stamens there are no sterile organs, which, according to Beccari, are appendages of the staminal connectives. There then remain *S. nana*, which for the above-mentioned reasons we will leave out of account for the present, *S. Arfakiana*, in which the segments of the male perianth terminate in appendages, which are here wanting, while the style in also fixed on the ovary in another way than in the specimen, with which we are here concerned, and *S. corniculata*. Of the characters, given by Beccari as typical of this latter species, all are found in the specimens from Java. I mention them here in succession. Small low plants, with somewhat strongly branched shoots and thick fleshy roots. Only the extreme tips of the shoot-branches bear flowers; of these the two or three lowest flowers are female, the upper ones male. The latter are present in larger numbers, but the uppermost generally remain buds. The perianth of the male flowers has six lobes and the latter are provided at their top with a few long fine hairs, resembling cilia; the filaments of the three stamens have more or less grown together. While the male flowers have definite, albeit short peduncles, the female flowers may well be described as sessile in the axil of a bract. Most characteristic are the pistils, which, as Beccari indicated, are sigma-shaped, while the upper part of the ovary and the style are more or less papillar; the description might perhaps still leave some doubt as to the identity, but the figures of ovary and fruit: 10, 11 and 12 are quite similar to the specimens in the Utrecht museum, as indeed all the other figures. Only the cilia at the top of the perianth leaves are figured somewhat shorter; this is, however, intelligible, as BECCARI had dried plants to work with and I had excellently preserved alcoholic material at my disposal.

My conclusion is therefore that the plants found in Tjiomas belong to *Sciaphila corniculata* BECCARI and that the distribution of this species is consequently not limited to New-Guinea, as BECCARI had imagined.

If we may now assume that the figures of *S. nana* given by BLUME are not very accurate — an assumption which does not seem to me to be very hazardous —, and if we further eliminate from BLUME's description the unbranched shoot, which was probably due to an accidental property of the specimen described, then it seems to me, that we may well assume, that *S. nana* of BLUME and *S. corniculata* of BECCARI are names for one and the same species, especially as so far no other species of this genus have become known from Java except the so widely different *S. tenella* BL.

There is however no complete certainty on this point, and as long as this is not the case, it will be best to affix the name of the accurately described *Sciaphila corniculata* BECCARI to the specimen in question, and for the present to regard the name of *Sciaphila nana* BL. as not sufficiently well characterized. Possibly a future monographer, having many more data at his disposal, will be able to restore this name, but at present it is better to reject it.

Utrecht, December 1908.

Astronomy. — "*The Solar Vortices of* HALE". By Mr. A. BRESTER Jz. Communicated by Prof. W. H. JULIUS.

On the more or less cyclonic configuration of the hydrogen flocculi around the spots on the spectroheliographs of the solar atmosphere and on the shifting and the becoming invisible of one of these flocculi at a short distance from a spot, HALE recently founded the hypothesis that the spots are vortices, which from the solar atmosphere continually absorb the hydrogen, which there comes back every time as new protuberances or flocculi outside the spots. [1])

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[1]) HALE: Astroph. Journ. Sept. 1908 — Contrib. from the Mt. Wilson Sol. Obs. No. 26.

At the outset I think I ought to observe that this hypothesis, which is considered by **Hale** himself, with the laudable caution characteristic of him, as still very uncertain [1]), is in a hardly explicable contradiction with the equality of the angular velocity of the hydrogen-flocculi in every latitude, which **Hale** has made probable in an earlier investigation [2]).

For if, between these flocculi and the spots there is the connection that **Hale** supposes, we should not expect the same angular velocity, at each latitude, but rather very different angular velocities, which would have to answer to the great aequatorial acceleration of the spots.

But the hypothesis that the spots are absorbing vortices, has often been proposed, but has always turned out very improbable. For a vortex leads us to expect first of all that it rotates. But generally nothing is seen of this rotation in the spots. **Carrington**, **Secchi** and **Young** have more than once intentionally set this forth. According to these observers some indication of a cyclonic configuration is shown in only 2 or 3 per cent of the spots, and this configuration is most times such that it would prove a rotation in opposite direction in different parts of a same spot and consequently an impossible rotation for the whole spot. [3]) Moreover **Mitchell** [4]) as well as **Hale** and **Adams**, [5]) in their investigations of the spot-spectrum, have found the gaseous substance of the spots generally in almost perfect rest. Besides the spots, as a rule, do not seem to be concave, but convex. [6])

Although these clear facts, which have been known a long time already, make it very improbable that the spots are to be considered as absorbing vortices, in **Hale**'s paper on "Solar Vortices" this improbability is demonstrated also in other ways. If there were in reality absorbing vortices above the spots, it would be impossible of course that their absorbing action would only be shown by a single one among the many flocculi which **Hale** saw floating above the spot studied by him. Yet we should have to believe in that impossibility, for among all the other flocculi above the spot **Hale** could not observe one, not even among the smallest and nearest to the spot, that showed the slightest advance towards the spot [1]).

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[1]) **Hale**: Contrib. 26 p. 14.

[2]) **Hale**: Astroph. Journ. April 1908.

[3]) **Young**: The Sun 1895 p. 126 — **Secchi**: Le Soleil I. p. 89.

[4]) **Mitchell**: Astroph. Journ. 22 p. 38.

[5]) **Hale** und **Adams**: Astroph. Journ. 25 p. 87.

[6]) Already at the first discovery of the spots **Christophorus Scheiner** drew the attention to their often occurring convexity and to their origin as through the bursting of bubbles. (Rosa Ursina 1626—1630 p. 461, 493, 513 etc.). See further: **Howlett**: M. N. Dec. 94 — Sidgreaves M. N. March. 95 — **Wilson**: M. N. 55 p. 458 — **Frost**: Astr. a. Astroph. II. p. 734 — **Maunder**: Journ. Br. Astr. Ass. 17 p. 128 — **Cortie**: Astroph. Journ. 7 p. 248 — **Moreux**: Bull. Soc. Astr. de France Janv. 1907.

In my opinion it is not at all certain even that this single dark flocculus, which **Hale** thought sufficient to prove the absorbing action of the Solar Vortices, actually disappeared in a spot. It is also quite possible that this flocculus, amidst other incessantly renewing and shifting flocculi, has been covered up by them in consequence of which it has become invisible. On very close and unprejudiced inspection, to be sure, we see that much of the quasi-absorbed flocculus is left on the clichés obtained after the supposed absorption.

But even more clearly than by the hydrogen flocculi the non-existence of material vortices is proved by the imperturbable rest of the calciumflocculi, which never show the least trace of a cyclonic configuration [3]), although according to **Hale** and also as appears from their angular velocity [2]), which Fox found to be somewhat smaller, they are probably even a little nearer to the spots than the hydrogen flocculi.

So it is on account of all these old and new direct evidences that I have come to the conviction that the spots are no material vortices. Neither the spectroheliographs of **Hale**, nor his discovery that there are lines in the spectrum of the spots, which most probably show the **Zeeman** effect [4]), have been able to indirectly weaken my conviction.

So, if, according to me the spots are no material vortices, but when the cyclonic configuration of the hydrogen-flocculi still reminds us in some degree of such vortices (vortices to be sure, according to **Hale** "so complex", I should prefer to say "so impossible" that, not unfrequently they show opposed motions in neighbouring places) [5]) we have now to explain how, also without material vortices, such a quasi-cyclonic configuration can originate.

A few years ago already I showed a way to come to that explanation, when I pointed out as follows how the Polar Auroras originate on the earth through the spots on the sun.[1] If we want to follow this explanation, we must suppose that there are radioactive substances on the sun. This supposition is surely not in the least extravagant, since we know how generally such substances are found on the earth and also take in consideration, how as a rule the same substances which we know on the earth, are also found on the sun. Moreover it is probable, also according to RUTHERFORD, that on the sun the radioactivity of matter will show itself even more energetically than on the earth, which is so much cooler.[2] If now there are radioactive substances on the sun — and also the presence of Helium is in favour of this — such substances will remain hidden under the photospherical shell, owing to their great weight, just as all other elements of great weight. So, under this shell their α, β and γ rays will originate. But for the greater part these rays will be prevented by this comparatively thick shell from escaping from the sun. Only where there are holes in this photospherical shell and so especially where we see spots, this impediment will not be so great. And so, out of each spot just as out of the leaden vessel in the investigations of Mrs. CURIE a bundle of more or less parallel β and γ rays will come forth, vertically going out into the wide world. If now such a bundle, which is often many times thicker than the earth, comes in contact with our atmosphere, it will bring here about all these electric and luminescence phenomena which have already been considered by BIRKELAND, PAULSEN and ARRHENIUS 1 as caused by kathode rays of the sun and 2 as the cause of our Polar Auroras and of our magnetic disturbances.[3]

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[1]) **Hale**: Contrib. 26 p. 15.

[2]) **Hale**: Astroph. Journ. April 1908. — **Fox**: Astroph. Journ. Sept. 1908.

[3]) **Hale**: Contrib. 26 p. 1, 6; Plate XXXVI.

[4]) Nature, Aug. 20 1908.

[5]) **Hale**: Contrib. 26 p. 6 "Although most of the points in a given region appear to move together, there are a sufficient number of apparently opposed motions to weaken seriously the value of the evidence".

If, by means of these supposed strong bundles of rays there is such a simple connection between these earthly phenomena and the cavities of the solar spots, we understand at once:

1. why these earthly phenomena have the same period of 11 years as the spots;

2. why also every year these earthly phenomena show maxima

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[1] De Nieuwe Courant 19 Febr. 1907 — Bull. Soc. Astr. de France Juin. 1907 p. 283 — Essai d'une Explication du Mécanisme de la Périodicité dans le Soleil et les Etoiles rouges variables. Verh. Kon. Akademie van Wetenschappen te Amsterdam IX. 6 p. 19—21 (1908).

[2] RUTHERFORD : Radioactivity 1904 p. 344 — MAUNDER : Knowledge Nov. 1903 p. 255.

[3] ARRHENIUS : Lehrb. d. Kosm. Physik. p. 152 — PAULSEN : Bull. Soc. Belge d'Astr. Oct. 1906 p. 381. See also my Essai of 1908 p. 20—23 referred to above.

in March and September and minima in June and December. (For the axis of the sun is in such a direction that in March and September those bundles of rays which are surest to reach us, are most numerous because then they are emitted from the parallels of $7\frac{1}{4}^\circ$ respectively southern and northern latitude, which are comparatively rich in spots, while such bundles occur most rarely in June and December, because then they must proceed from the equator which has very few spots).

3. why these earthly phenomena also have a period of 27 days which agree with the synodical rotation of the spots, and

4. why also these earthly phenomena often become more powerful suddenly, when a great spot appears on the sun.

My hypothesis that Polar auroras will originate here when bundles of β and γ rays thrown out by the solar spots reach our atmosphere, is considerably strengthened by the important fact discovered by Sir and Lady HUGGINS, that when also here in our laboratories the rays of Radium come in contact with our atmosphere, they cause in it a luminescence, which spectroscopically show the same four nitrogen lines, which have also been found among the most important of the Polar Aurora by PAULSEN 1)).

Though the Polar Aurora shows many distinct phenomena, which agree very well with my explanation of its origin, it also shows many other phenomena, which, although very mysterious still, are also of the highest importance for the theory of the sun. Such mysterious phenomena are the rapid motions which the light configurations of the Polar Auroras so often show. What it is that in the Polar Auroras causes their bows to wave, their curtains to fly, their brilliant sea of flames to trill, their bundles of rays to flash out suddenly, we do not know. But we do know (and that is the thing really of the greatest importance for the theory of the sun) that all these rapid motions cannot be ascribed to material changes of place. In the time of VON HUMBOLDT, who tells it to us 2)), the inhabitants of the Shetland Islands may have considered such motions as caused by a "merry dance in Heaven"; the astronomers may still go on taking rapidly appearing rays on the sun for "terrible eruptions", here on our calm earth such fantastic speculations are

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1) Sir W. HUGGINS a. Lady HUGGINS.: Astroph Journ. Sept. 1903. On the spectrum of the spontaneous luminous Radiation of Radium at ordinary temperatures. — The four nitrogen lines photographed in this investigation and found among the most important of the Polar Aurora by PAULSEN are the lines 3372, 3575, 3918 and 4285. ARRHENIUS: loc. cit. p. 910.

2) v. HUMBOLDT: Kosmos 1st vol. 2nd part p. 200.

too naive. For us it is impossible to see material eruptions in the bundles of the auroral rays which often shoot up as quick as lightning. In all such sudden shiftings of light the molecules of our atmosphere remain comparatively at rest and probably it is only electrons or ions that move.

But if our Polar Auroras are such movable electric configurations, which originate when bundles of β and γ rays, sent out by the solar spots, come in contact with our atmosphere, then it is quite conceivable that analogous movable configurations will originate also in the solar atmosphere itself around the spots, if there these same bundles, just escaped from the spots and consequently much more powerful even than here, pass through the solar atmosphere. Thus the Protuberances of the sun and the rays of its Corona would have the same cause as the Polar Auroras of the earth and the "Solar Vortices" of HALE would be "Solar Aurorae". In all these phenomena only ions would move, and, as I have already maintained these 20 years [1]), the matter would remain at rest.

For that identical origin of on the one side the Protuberances and the Corona of the sun and on the other side the Polar Auroras on the Earth, which identical origin I have already discussed in my last Essai [2]), pleads also the remarkable agreement, which STASSANO discovered in the spectra of these three sources of light. **Stassano** has found, that while $\frac{2}{3}$ of the lines in the spectrum of the Polar Aurora must be ascribed to Neon, Argon, Krypton and Xenon, also the light of the Protuberances and especially of the Corona greatly emanates from the same newly discovered elements of the Zero-group. Among the spectral lines, which have been found in the Protuberances by **Deslandres** and **Hale**, there are, according to **Stassano**, 44 which belong to this Zero-group and nearly all the 339 corona lines, photographed by **Humphreys** during the eclipse of 1901, are also lines of this group. [1]) And so it is the same elements which (according to me also for the same reason) cause the same light to shine on the outside of the sun and the earth.

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[1]) As the fundamental principle of my theory of the sun I have always demonstrated the impossibility of the dogma of the solar eruptions. That demonstration will be found and will be seen to become more and more powerful in the following papers: Verklaring van de veranderlijkheid der roode sterren p. 9—11. (Mei 1888) — Essai d'une Théorie du Soleil et des étoiles rouges variables p. 20 (Dec. 1888) — Théorie du Soleil. Verhandelingen Kon. Akad. v. Wetensch. te Amsterdam I. No. 3. p. 1—30 (1892) — Astron. a. Astrophysics Dec. 1903, March 1894 p. 218, Dec. 1894 p. 849. — My last Essai of 1908 referred to above p. 1—31. Het 17de Jaarverslag van het Technologisch Gezelschap te Delft. p. 87—124, Een theorie van de zon.

[2]) Essai d'une Explication du Mécanisme de la périodicité etc. 1908 p. 20—23, 84, 125. In this my last Essai I have shown on p. 21, that, if the solar spots throw out the bundles of rays which I suppose, it is very clear why the same period of 11 years of the solar spots is also observed in the 3 following luminescence-phenomena; 1. in the protuberances and the corona of the sun, 2. in the Polar Auroras on the earth and 3. in the Comets. Thus it appeared in the investigations of BERBERICH that during the maximum period of the spots (so, when the Comets have the greatest chance of being brought to greater luminescence by the bundles of rays meant by me) the radiance of the Comet of ENCKE is greatest and that then also the discovery of very small Comets is most successful. (Astron. Nachr. n°. 2836 and 2837). The sudden variations of light, which the Comets sometimes show and which now have been seen again so distinctly in the Comet of MOREHOUSE, may also be explained perhaps by their temporary contact with the bundles of rays thrown out by the solar spots. On the same page 21 of my

If there is therefore great reason to take **Hale**'s "Solar Vortices" for Solar Aurorae, the configurations and the motions of the hydrogen-flocculi in these Vortices do not at all clash with the improbability of the existence of material vortices.

For these flocculi then agree with the electric light configurations of our Polar Auroras and like these they will move without any change in the place of the molecular matter.

Hale's Solar Vortices instead of weakening my idea about the rest of the sun, give on the contrary unexpectedly a splendid support to this idea. For they help to remove the principal objection, which has always wrongly been raised against this idea and has been derived from the shifting of the spectral lines. For if, for the many reasons developed above, we consider these Vortices as Aurorae, they lead us to the conclusion that, although a gas is at rest, yet it will show shifted spectral lines, if only it contains enough ions rapidly moving in the line of sight. The correctness of this conclusion, at which, on other grounds also **Schuster** has lately arrived, [2]) was a few years ago experimentally proved by **Stark**, when, in examining the light of hydrogen in the

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Essai is also illustrated the characteristic change of shape of the corona with the period, and the rays of the corona are not taken for real eruptions (as **Schaeberle** does), but for luminescences, analogous to the rays of the Polar Aurora. In my Essai (p. 84—88) has also been treated the repartition of the Protuberances, little agreeing with the repartition of visible spots. Openings, too small to be seen as spots throw out nevertheless their bundles of rays which form their Protuberances. If now these openings, as my theory tries to demonstrate, are smallest at a latitude from 60 to 65°, then with that the constant minimum of the Protuberances at this latitude is explained too.

[1]) **Arrhenius**: Lehrb. d. Kosm. Physik. p. 911.

[2]) **Schuster**: Nature 29 Oct. 1908.

direction of channel rays which he led through it, he photographed at the same time 1. the normal lines of the hydrogen at rest and 2. the strongly shifted lines of the hydrogen-ions in motion.[1]

And so finally it appears that the relative tranquillity of the sun, never disturbed by terrible eruptions, as has been proved so clearly by numerous important solar phenomena and has been demonstrated especially also in the last year by the rotation-investigations of ADAMS, HALE and FOX,[2] is not even in contradiction with a DOPPLER shifting of the spectral lines of the Protuberances.

Delft, the 1st of January, 1909.

Physics. — "*On the course of the isobars of binary mixtures.*"

By Prof. PH. KOHNSTAMM. Communicated by Prof. J. D. VAN DER WAALS.

1. In these Proceedings of June 27th 1908 VAN DER WAALS showed that only if $a^2_{12} < a_1 a_2$ the curves $\frac{dp}{dx} = 0$ and $\frac{dp}{dv} = 0$ can touch for volumes larger than $3b$, the critical volume of the mixture taken as homogeneous. On the supposition $a_1 a_2 = a^2_{12}$ the point of contact lies at a value $v = b$. Now at higher temperature the well-known diagram of isobars (These Proc. IX p. 630) leads to the intersection of the two branches of $\frac{dp}{dv} = 0$ on the line $\frac{d^2p}{dv\,dx} = 0$, which takes place at the minimum critical temperature of the system under discussion. Then the line $\frac{dp}{dv} = 0$ divides into two branches, which we can now denote as the lefthand branch and the righthand branch. The lefthand branch necessarily intersects the line $\frac{dp}{dx} = 0$ in two points, and as it contracts more and more, while the line $\frac{dp}{dx} = 0$ moves towards the right with increase of temperature — the asymptote of this locus being given by $\frac{da}{dx} = MRT\frac{db}{dx}$ — contact must take place, and that for a volume larger than that for which the line

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[1] STARK: Astroph. Journ. Dec. 1906, p. 362.

[2] ADAMS: Astroph. J. November 1907, April 1908. — HALE: ibid. April 1908. — FOX: ibid. Sept. 1908.

$\frac{dp}{dv}=0$ has its tangent parallel to the v-axis, and which is therefore larger than $3b$. So it would seem to follow from this diagram of isobars, in connection with the just-mentioned theorem of VAN DER WAALS that the possibility of a minimum critical temperature is excluded on the supposition $a_1a_2=a^2_{12}$. However, already in his Théorie Moléculaire VAN DER WAALS derived the condition for the existence of a minimum critical temperature, viz.:

$$\frac{a_{12}}{b_{12}}<\frac{a_1}{b_1} \text{ and } \frac{a_{12}}{b_{12}}<\frac{a_2}{b_2} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

It is clear that it is easy to satisfy this condition also in the case of $a^2_{12}=a_1a_2$, e.g. — if we assume [1]) $2b_{12}=(b_1+b_2)$ — by the values $b_2=3b_1$ and $a_2=3a_1$, from which $b_{12}=2b_1$, $a_{12}=a_1\sqrt{3}$, so that the two conditions (1) become:

$$\frac{1}{2}\sqrt{3}<1.$$

Now it is true that the case will not easily occur that of two substances which have the same critical temperature, the one has molecules three times as large as those of the other, and a physical theory which does not intend to investigate all mathematically possible combinations of a's and b's, but only those which really occur, need perhaps hardly consider this point. It would indeed be very desirable for us to have an insight into the way in which the a's and b's of simple substances are connected, and for mixtures into the way in which a_{12} is connected with the a's of the components, so that the theory of the mixtures need only reckon with realisable combinations. Now, however, we do not possess this knowledge, and it seems hardly possible as yet to indicate in what direction such an insight might be gained. Under these circumstances it seems to me most advisable to develop as completely as possible the conclusions which proceed from the different possible suppositions for the dependence of a_{12} on a_1 and a_2, and to compare these results with the results of observation, in order to try and get an indication in this way of the last-mentioned dependence. No doubt we shall treat a great many suppositions and combinations in this way which will appear to be of no physical signification, but it seems to me that under the given circumstances this difficulty is unavoidable. In this sense the following investigations concerning diagrams of isobars, deviating from those examined up to now and cited above, are to be considered.

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[1]) In fact we must do so, because the theorem of VAN DER WAALS mentioned only holds for this supposition.

2. It appears from the fact mentioned in 1 viz. that the diagram of isobars of fig. 1 loc. cit. in connection with the theorem of VAN DER WAALS mentioned excludes the possibility of a minimum critical temperature for the case $a_{12} = a_1 a_2$, whereas after all also on this supposition a minimum critical temperature is not impossible, that the diagram of isobars mentioned is not the only one possible. Now the shape of this diagram is in the first place controlled by the line $\frac{dp}{dx} = 0$, and the question suggests itself if in general another shape of this line is also conceivable. In the determination of its course it was derived from the equation:

$$\frac{v^2}{(v-b)^2} = \frac{\frac{da}{dx}}{MRT\frac{db}{dx}}$$

that an asymptote must exist for the value of x determined by:

$$\frac{da}{dx} = MRT\frac{db}{dx}$$

and that to the right of this point everywhere a positive value of v greater than b is to be found satisfying this equation. In this it has been tacitly assumed that for the value of x, for which $\frac{da}{dx} = MRT\frac{db}{dx}$, b is still positive; for if b were negative at this place, only a high *negative* value of v could satisfy for the values of x somewhat larger than that for which $\frac{da}{dx} = MRT\frac{db}{dx}$, and hence the course of $\frac{dp}{dx} = 0$ would become an altogether different one. So though naturally that value of x for which b becomes $= 0$, can never lie within the realisable part of the diagram of isobars, it yet appears that the situation of this point can determine the course of $\frac{dp}{dx} = 0$ and with it of the isobars in the realisable region.

3. In the complete (extended) diagram of isobars such a point must probably always occur. This is self-evident if we should be justified in considering the dependence of b on x as linear, and it is also easy to show it if we assume LORENTZ's well-known formula for b_{12}. For then:

$$b_{12} = \left(\frac{\sqrt[3]{b_1} + \sqrt[3]{b_2}}{2}\right)^3$$

and we have to prove that this value is larger than $\sqrt{b_1 b_2}$. If we now put $b_2 = n^6 b_1$, the condition which is to be satisfied, is:

$$\frac{n^6+3n^4+3n^2+1}{8} > n^3$$

or

$$n^6 + 3n^4 - 8n^3 + 3n^2 + 1 > 0$$

or

$$(n-1)^2 (n^4 + 2n^3 + 6n^2 + 2n + 1) > 0.$$

It is clear that for positive values of n this condition is always fulfilled, so that $b_{12}^2 > b_1 b_2$, and the equation:

$$b_1 (1-x)^2 + 2b_{12}\, x (1-x) + b_2 x^2 = 0$$

has always real roots.

4. It has now been assumed in the general diagram of isobars (loc cit.) that these roots always lie on the leftside of that value of x for which $\frac{da}{dx} = 0$. To what change will this diagram be subjected in the opposite case? We begin with determining the course of $\frac{dp}{dx} = 0$ in this case. So as $\frac{da}{dx}$ is positive, according to our supposition, for that value of x for which $b = 0$, we can always think the temperature so low that for this value of x, which we shall call x_0:

$$n = \frac{MRT \frac{db}{dx}}{\frac{da}{dx}} < 1$$

Then we get for the course of $\frac{dp}{dx} = 0$ in the neighbourhood of x_0

$$\frac{v-b}{v} = \pm \sqrt{n} \text{ or } v(1 \pm \sqrt{n}) = b \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now the value of b is positive for somewhat higher value of x than x_0, whereas b becomes negative for somewhat smaller value of x. So we see that two branches of $\frac{dp}{dx} = 0$ pass through the point $x = x_0$, $v = 0$. The two branches lie on either side of the line $v = b$, and have both positive v for $x > x_0$, negative v for $x < x_0$. Neither of the branches touch the line $v = b$, but as follows from (2), both form an angle with it, which is the greater as n approaches closer to 1. This last result may be verified by a direct determination of the direction. For:

$$\left(\frac{dv}{dx}\right)_{\frac{dp}{dx}=0} = -\frac{\dfrac{d^2p}{dx^2}}{\dfrac{d^2p}{dvdx}} = \frac{\dfrac{2MRT}{(v-b)^3}\left(\dfrac{db}{dx}\right)^2 + \dfrac{MRT\dfrac{d^2b}{dx^2}}{(v-b)^2} - \dfrac{\dfrac{d^2a}{ax^2}}{v^2}}{\dfrac{2MRT}{(v-b)^3}\dfrac{db}{dx} - \dfrac{2\dfrac{da}{dx}}{v^3}} =$$

$$= \frac{2MRT\left(\dfrac{db}{dx}\right)^2 - \dfrac{(v-b)^3}{v^3}\dfrac{d^2a}{dx^2} + MRT\dfrac{\dfrac{d^2b}{dx^2}}{\dfrac{db}{dx}}(v-b)}{2MRT\dfrac{db}{dx} - 2\dfrac{da}{dx}\left(\dfrac{v-b}{v}\right)^3} =$$

$$= \frac{\dfrac{db}{dx} \pm \dfrac{nv\sqrt{n}}{2MRT}\dfrac{\dfrac{d^2a}{dx^2}}{\left(\dfrac{db}{dx}\right)^2} + \dfrac{1}{2}\dfrac{\dfrac{d^2b}{dx^2}}{\dfrac{db}{dx}}(v-b)}{1 \pm \sqrt{n}} = \frac{\dfrac{db}{dx}}{1 \pm \sqrt{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

because the second and the third member of the numerator vanish when we approach $v=0$.

It is clear that $\frac{dp}{dx}=0$ has again an asymptote for that value of x, for which $\frac{da}{dx}=MRT\frac{db}{dx}$, while no points of $\frac{dp}{dx}=0$ are found on the leftside of $\frac{da}{dx}=0$, at least as long as we are on the righthand side of the point $\frac{db}{dx}=0$ on the supposition of a quadratic function for b. Now too $\frac{dp}{dx}=0$ will approach asymptotically to the line $v=b$ on the righthand side of the diagram, when we assume the linear form for b. If we accept the quadratic form for b, $\frac{dp}{dx}=0$ approaches asymptotically to a line found from $v=b$ by multiplying all the coordinates by:

$$\frac{1}{1+\dfrac{MRT\,(b_1+b_2-2b_{12})}{a_1+a_2-2a_{12}}}$$

From all these data follows the form for $\frac{dp}{dx}=0$ indicated in fig. 1.

If we take the temperature higher, so that for $x = x_0$:

$$\frac{MRT\dfrac{db}{dx}}{\dfrac{da}{dx}} > 1$$

this shape is reduced to a shape which, as regards its realizable part, agrees perfectly with the ordinary one. For then there is an

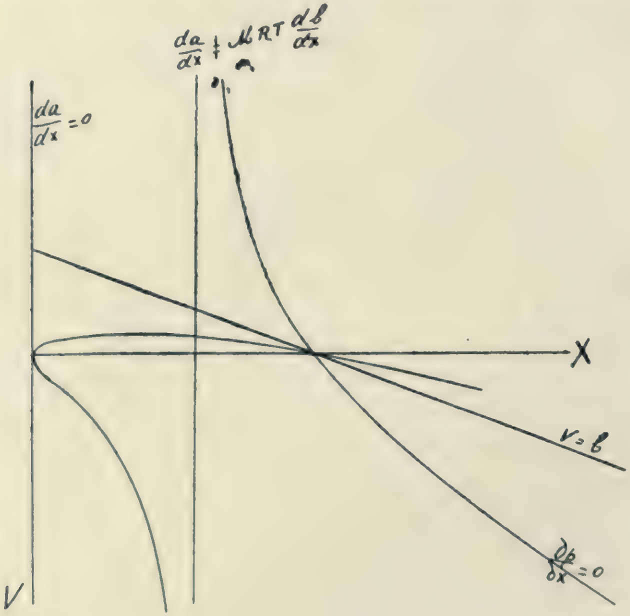

Fig. 1.

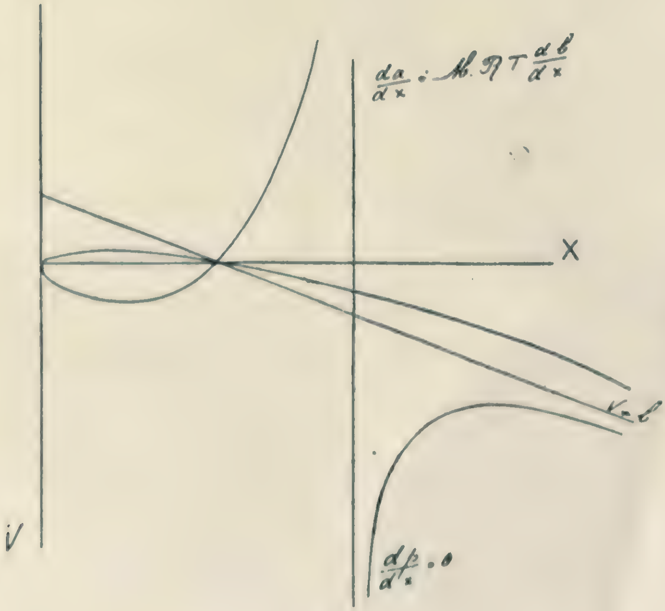

Fig. 2.

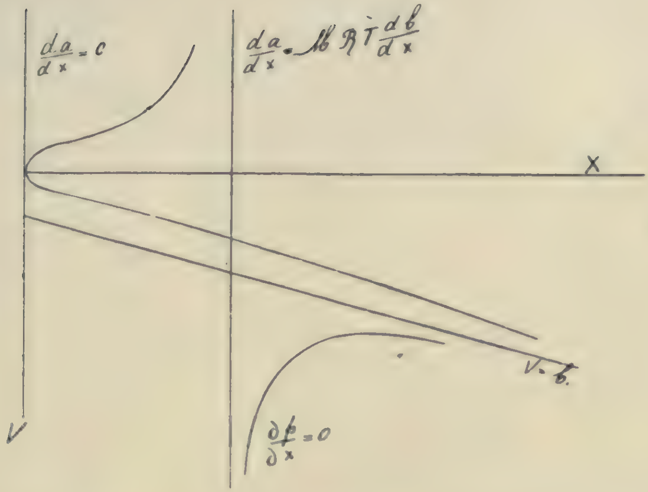
$\frac{da}{dx} = c$
$\frac{da}{dx} = MRT\frac{db}{dx}$
X
V
$v = b.$
$\frac{\partial p}{\partial x} = 0$

Fig. 3.

asymptote on the right of x_0, viz. where $\frac{da}{dx} = MRT\frac{db}{dx}$. The course in the double point $x = x_0$, $v = 0$ now follows again from (2), provided it is borne in mind that now $n > 1$. (See fig. 2). For comparison we reproduce the complete diagram for the ordinary case in fig. 3, which will not require any elucidation. Only the transition temperature between fig. 1 and 2, for which $\frac{da}{dx} = MRT\frac{db}{dx}$ just at $x = x_0$, calls for discussion. To simplify the calculation we introduce as origin of the coordinates the point $x = x_0$, $v = 0$; in its neighbourhood we may put:

$$\frac{da}{dx} = MRT\frac{db}{dx} + MRT\frac{db}{dx}C_1x$$

and

$$b = C_2x$$

where

$$C_1 = \frac{\frac{d^2a}{dx^2}}{MRT\frac{db}{dx}}$$

and

$$C_2 = \frac{db}{dx}$$

so that the equation for $\frac{dp}{dx} = 0$ becomes:

$$\left(\frac{v - C_2x}{v}\right)^2 = \frac{1}{1 + C_1x} = 1 - C_1x$$

if we neglect the second powers, from which follows for the two roots:

$$1-\frac{C_2x}{v}=1-\frac{C_1x}{2} \qquad 1-\frac{C_2x}{v}=-1+\frac{C_1x}{2}$$

$$v_1=\frac{2C_1}{C_1}=\frac{2MRT\left(\frac{db}{dx}\right)^2}{\frac{d^2a}{dx^2}} \quad v_2=\frac{C_2x}{2}=\frac{1}{2}b\,.$$

So we have one finite root and one root equal to zero from which follows fig. 4 for the course of $\frac{dp}{dx}=0$.

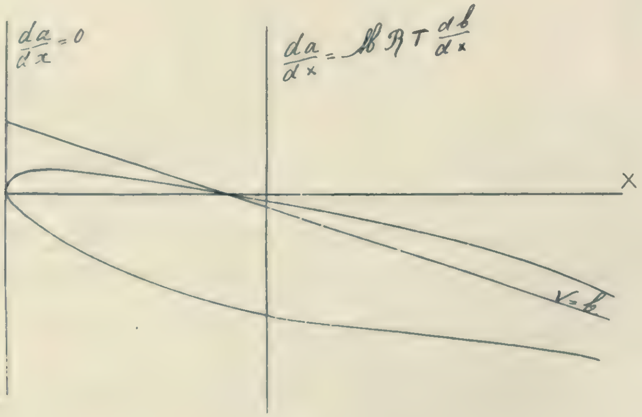

Fig. 4.

5. In the second place we have to examine the course of $\frac{dp}{dv}=0$ in the case now under consideration. We may write the equation of this curve in the form:

$$MRT\,v^3-2a\,(v-b)^2=0.$$

It is very easy to separate the roots of this equation. For, when a is positive, the first member is negative for $v=0$, positive for $v=b$, and positive for $v=\infty$. So there is a root between 0 and b, and either two or none for $v>b$, as is known, according as the critical temperature is below or above the critical temperature for the mixture under consideration. When b becomes equal to 0, both the product of the three roots and the sum of the products taken by twos becomes equal to zero. So there are two roots $v=0$ in this case. And the third root assuming the value $\frac{2a}{MRT}$, the two branches passing through the point $x = x_0$, $v = 0$, appear to be the liquid branch and the branch $v < b$, which has no physical signification. These two branches touch the line $v = b$ in the point mentioned as appears from the fact, that the product of these two roots is in the neighbourhood of this point b^2, and the sum of these roots $2b$. Besides we can also prove this directly from the direction of the tangent. For:

$$\left(\frac{dv}{dx}\right)_{\frac{dv}{dv}=0} = -\frac{\frac{d^2p}{dvdx}}{\frac{d^2p}{dv^2}} = \frac{\frac{2MRT}{(v-b)^3}\frac{db}{dx} - \frac{2\frac{da}{dx}}{v^3}}{\frac{2MRT}{(v-b)^3} - \frac{6a}{v^4}}$$

If we substitute in this equation the value for $(v-b)$ from the equation for $\frac{dp}{dv} = 0$, we get:

$$\left(\frac{dv}{dx}\right)_{\frac{dp}{dv}=0} = \frac{2MRT\frac{db}{dx} - 2\frac{\left(\frac{MRT}{2a}\right)^{3/2} v^{9/2}}{v^3}}{2MRT - \frac{6a\left(\frac{MRT}{2a}\right)^{3/2} v^{9/2}}{v^4}}$$

When we approach $v = 0$ the second members disappear in numerator and denominator, so that we keep:

$$\left[\left(\frac{dv}{dx}\right)_{\frac{dp}{dv}=0}\right]_{v=0} = \left[\frac{db}{dx}\right]_{b=0}$$

So for x little greater than x_0, $\frac{dp}{dx} = 0$ will have greater volume than $\frac{dp}{dv} = 0$ for the same x. If, however, there should occur a minimum critical temperature in the system, and we shall see later on that this is very possible, there will be a point of intersection of $\frac{dp}{dx} = 0$ and $\frac{dp}{dv} = 0$, which will, of course, constitute a fundamental point for the diagram of isobars.

Before proceeding to a discussion of the shape of the isobars themselves, we shall have to indicate for a complete elucidation of the problem discussed in the beginning, which gave rise to this investigation, in what way the lines $\frac{dp}{dx}=0$ and $\frac{dp}{dv}=0$ get quite detached in this case. For this purpose we must ascertain what the relative position of these two curves will be at the temperature, at which $\frac{da}{dx}=MRT\frac{db}{dx}$ just for x_0, and for which, therefore, fig. 4 holds. Now slightly on the right of x_0, where b has very small values without a approaching to zero, the critical temperature is very high, so the two branches of $\frac{dp}{dv}=0$ well certainly still exist on the right of x_0. But this curve will be closed towards the righthand side, i.e. passing from x_0 to the right we shall first have mixtures which are below their critical temperature at the temperature considered, then mixtures which are already above it, and still further to the right we may sometimes meet with mixtures which are again below their critical temperature, sometimes not.

6. It is very easy to prove this on the supposition $b_{12}=\frac{1}{2}(b_1+b_2)$. In this supposition we can give a very simple construction for the mixture with minimum critical temperature. Let the curve on which A lies (fig. 5) represent the values of a, the right line BD the values of b, then:

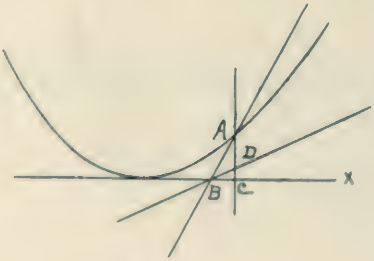

Fig. 5.

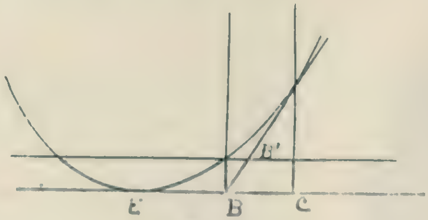

Fig. 6.

$$tg\,ABC=\frac{a}{b}\,tg\,DBC$$

in the point A.

As $tg\,DBC$ is constant, $tg\,ABC$ is minimum if $\frac{a}{b}$ is minimum; hence we find the mixture with minimum critical temperature by tracing a tangent to the curve from B. For this point of contact:

$$\left(\frac{da}{dx}\right)_C=\frac{27}{8}MRT_m\frac{db}{dx}.$$

According to a well known property of the parabola the point B lies halfway between E and C, (fig. 6), and $\frac{da}{dx}$ being equal to zero in E, and increasing linearly with x:

$$\left(\frac{da}{dx}\right)_B = \frac{1}{2}\left(\frac{da}{dx}\right)_C = \frac{27}{16} MRT_m \frac{db}{dx}.$$

So for the asymptote of $\frac{dp}{dx} = 0$ to be found in B, so $\left(\frac{da}{dx}\right)_B = MRT \frac{db}{dx}$ we must raise the temperature to $\frac{27}{16} T_m$. A fortiori the thesis holds, of course, if, instead of $a_{12}{}^2 = a_1 a_2$, as was put here, $a_{12}{}^2 > a_1 a_2$. For instead of the combination of the curve with the right line EBC we get then the combination of the first-mentioned with the right line through B', and B' lying to the right of B, the temperature will have to be raised still higher than just now, for $\frac{da}{dx}$ to be $= MRT \frac{db}{dx}$ in the point B'.

Also in the general case for b we can demonstrate the property mentioned, and it will appear afterwards that for these general considerations it is desirable not to replace the quadratic form of b unnecessarily by the linear one. We treat the case $a_{12}{}^2 > a_1 a_2$ at once, so that $a = 0$ has two real roots. We choose the point B' as origin; we call the abscissae of the points where $\frac{db}{dx} = 0$, $\frac{da}{dx} = 0$ and $a = 0$ in absolute value resp. x_1, x_2, x_3, then we can write the equations for a and b (see fig. 7):

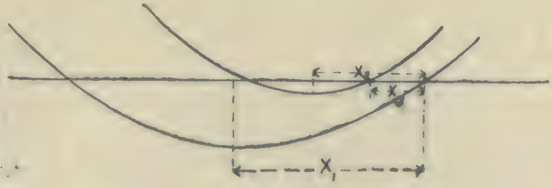

Fig. 7.

$$a = a_1 (x + x_2)^2 - a_1 (x_2 - x_3)^2 = a_1 (x^2 + 2x\, x_2 + 2x_2 x_3 - x_3{}^2)$$
$$b = b_1 (x + x_1)^2 - b_1\, x_1{}^2 = b_1\, x^2 + 2b_1\, x_1\, x$$

The temperature at which the asymptote of $\frac{dp}{dx} = 0$ reaches the point B' is determined by:

$$MRT = \left[\frac{\frac{da}{dx}}{\frac{db}{dx}}\right]_{x=0} = \frac{a_1 x_2}{b_1 x_1}.$$

Now we must investigate if there exist mixtures for which this temperature is the critical one on the right of B'. And so:

$$\frac{a_1 x_2}{b_1 x_1} = MRT = \frac{8}{27}\frac{a}{b} = \frac{8}{27}\frac{a_1\,(x^2+2xx_2+2x_2x_3-x_3^2)}{b_1\,(x^2+2xx_1)}.$$

So for the determination of x we find the equation:

$$x^2\left(x_2-\frac{8}{27}x_1\right)+\frac{38}{27}x_1x_2\,x-\frac{8}{27}x_1x_3\,(2x_2-x_3)=0.$$

If for the sake of brevity we call the coefficient of x^2 A, the roots are:

$$x=-\frac{19}{27}\frac{x_1x_2}{A}\pm\frac{1}{A}\sqrt{\frac{19^2}{27^2}x_1^2x_2^2+\frac{8}{27}A\,x_1x_3\,(2x_2-x_3)}$$

If A is positive, the roots are real, as according to the supposition x_2 is $> x_3$, and the expression under the radical sign being larger than $\frac{19}{27}x_1x_2$, we get a positive and a negative root. So this means that one mixture on the right of B' has its critical temperature at the said temperature. Hence the line $\frac{dp}{dv}=0$ has a direction // v-axis at this x, and $\frac{dp}{dv}=0$ does not exist any longer on the right of this mixture.

If A is negative, both roots remain real, for then we get under the radical sign:

$$\frac{19^2}{27^2}x_1^2x_2^2+\frac{8}{27}x_1x_2x_3\,(2x_2-x_3)-\frac{128}{27^2}x_1^2x_2x_3+\frac{64}{27^2}x_1^2x_3^2$$

As $x_2 > x_3$ the second term is positive, and the third is smaller than the first. So the expression under the radical sign is positive, but smaller than $\frac{19}{27}x_1x_2$. The first term of the expression for the roots now being positive, we have now two positive values of x, i. e. on the left of B' we have first a region of mixtures which are below their critical temperature, then a region of mixtures which are already above it, and on this follows again a region of mixtures below their critical temperature. So the line

$\frac{dp}{dv}=0$ has split up into two branches. We need not concern ourselves about the righthand branch at least now, for the detaching of $\frac{dp}{dx}=0$ and $\frac{dp}{dv}=0$. For the point with minimum volume of this branch — which has the well-known shape — lies on the line $\frac{d^2p}{dvdx}=0$, and so at greater volume than $\frac{dp}{dx}=0$. The line $\frac{dp}{dx}=0$ can, therefore, intersect this rightside part only in the branch of the two curves where $\frac{dv}{dx}>0$, and this intersection does not offer anything noteworthy for our present investigation. So we have only to examine how $\frac{dp}{dx}=0$ intersects the leftside half of $\frac{dp}{dv}=0$ and detaches itself from this left side half or the only one that is left at this temperature in the case just discussed that A is positive.

7. Now we saw before that in fig. 4 the point where $\frac{dp}{dx}=0$ intersects the line $x=x_0$, lies at a value of v:

$$v_1=\frac{2\,MRT\left(\frac{db}{dx}\right)^2}{\frac{d^2a}{dx^2}}.$$

At a temperature somewhat but very little lower, $\frac{dp}{dx}=0$ will have nearly the same course on the right of $x=x_0$ as in fig. 4, then, very near the value $x=x_0$, $v=v_1$ it will abruptly turn upwards and pass through the point $x=x_0$, $v=0$. This follows also from the coefficient of direction, which approaches ∞ according to formula (3). At somewhat higher temperature the first part will remain almost unchanged, but the curve, having got very near $x=x_0$, $v=v_1$ will now turn abruptly downward to an asymptote lying somewhat to the right of x_0. So the question whether for this temperature a double intersection of $\frac{dp}{dx}=0$ and $\frac{dp}{dv}=0$ will exist, which will necessarily lead to a contact afterwards, before the curves get quite detached, is entirely dependent on the fact whether the point $x = x_0$, $v = v_1$ lies outside or inside $\frac{dp}{dv} = 0$ for the temperature considered, as appears clearly from the figs. 8 and 9. Now as we saw before the point where $\frac{dp}{dv} = 0$ intersects the line $x = x_0$ is determined by:

$$v_2 = \frac{2a}{MRT}$$

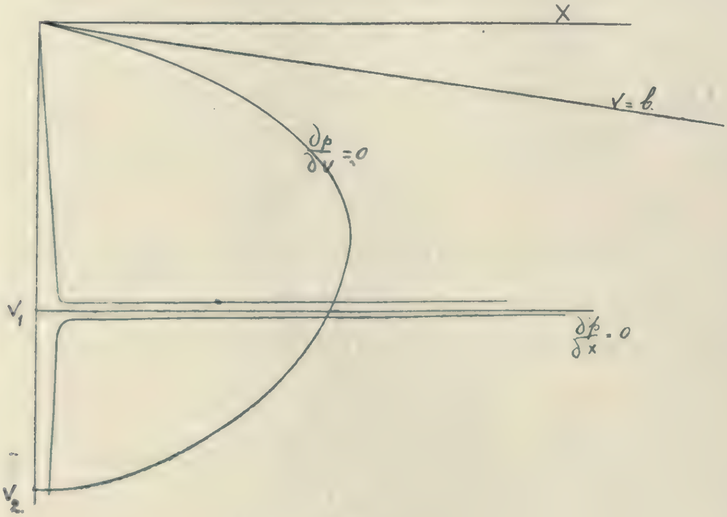
X
$v = b$
$\frac{\partial p}{\partial v} = 0$
v_1
$\frac{\partial p}{\partial x} = 0$
v_2

Fig. 8.

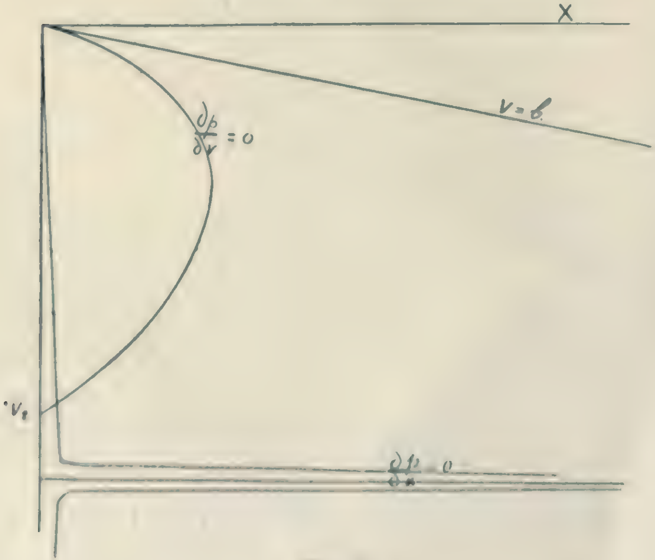
X
$v = b$
$\frac{\partial p}{\partial v} = 0$
v_2
$\frac{\partial p}{\partial x} = 0$

Fig. 9.

Accordingly the question whether for a temperature somewhat higher than that for which for x_0 $\frac{da}{dx} = MRT\frac{db}{dx}$, there will be double intersection and then contact, or no intersection of the two curves, will depend on the fact whether the expression :

$$\frac{v_1}{v_2} = \frac{\dfrac{2MRT\left(\dfrac{db}{dx}\right)^2}{\dfrac{d^2a}{dx^2}}}{\dfrac{2a}{MRT}}$$

or, since we have here $\frac{da}{dx} = MRT\frac{db}{dx}$:

$$\frac{v_1}{v_2} = \frac{\left(\dfrac{da}{dx}\right)^2}{a\dfrac{d^2a}{dx^2}} = \frac{2\left(\dfrac{da}{dx}\right)^2}{4(a_1a_2-a^2_{12})+\left(\dfrac{da}{dx}\right)^2}$$

will be smaller or larger than 1. So for the case $a_1a_2 = a^2_{12}$ there is no longer any question of intersection above the temperature

$$MRT = \left[\frac{\dfrac{da}{dx}}{\dfrac{db}{dx}}\right]_{x=x_0}$$

because then v_1 is twice as large as v_2, and a_{12} must have considerably descended below this value, before there can be question of this. Just as VAN DER WAALS derived (These Proc. June 1908) we get contact if $v_1 = v_2$, and so

$$\frac{\left(\dfrac{da}{dx}\right)^2}{a\dfrac{d^2a}{dx^2}} = 1.$$

It appears that the value of $\frac{b}{v}$, which belongs to the point of contact (loc. cit. fig. 32) becomes equal to zero in this case, not because the denominator becomes infinite, but because the numerator becomes zero.

In a subsequent communication I hope to indicate the course of the isobars in the case given here, and to examine by the aid of a general survey of the possible combinations of a's and b's,, whether besides the diagram of isobars given by VAN DER WAALS and the one treated here there are other diagrams of isobars possible for mixtures of normal substances with a's and b's which are quadratic functions of x.

ERRATUM.

p. 294 line 20 *read* $6|b\,a\,d\,c$, *for* $6|b\,c\,d\,a$.
,, 22 *read* $8|d\,c\,b\,a$, *for* $8|d\,a\,b\,c$.

(February 25, 1909).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday February 27, 1909.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 27 Februari 1909, Dl. XVII).

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Chemistry. — "*The system: Copper sulphate, Copper chloride, Ammonium sulphate, Ammonium chloride and Water at* 30°". By Prof. F. A. H. Schreinemakers.

(Communicated in the Meeting of January 30, 1909).

Although the above mentioned five substances take part in the construction of this system only four need be considered as components, as between the four salts exists the relation;

$$CuSO_4 + 2NH_4Cl = (NH_4)_2SO_4 + CuCl_2.$$

The system constructed from the four salts only ought, therefore, to be looked upon as a ternary one; we will now see first of all how we may represent such a system.

Let us take the four substances: *AB*, *AC*, *BD* and *CD* between which may take place the double decomposition:

$$AB + CD = AC + BD$$

If we represent the substances *AB*, *AC* and *BD* by the angles of a rectangular isoxeles triangle the rectangular side of which has the length 1 [fig. 1] substance *CD* is represented by the point *CD* so situated that the four points representing the four substances form the angles of a tetragon. What will now be the composition of a

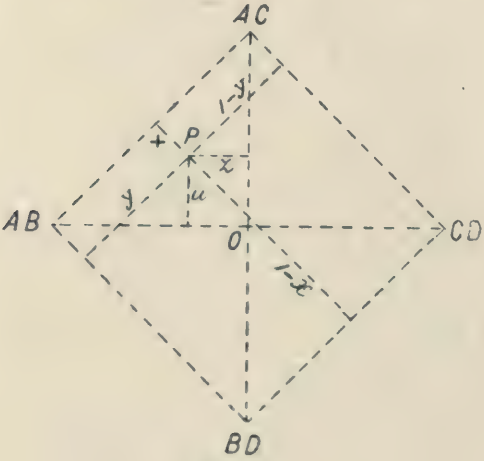

Fig. 1.

phase represented by point p? This may be represented in various manners according to the nature of the three substances in which it has to be expressed.

1. We take as components *AB*, *AC* and *BD*.

The point p then represents x Mol. *BD*, y Mol. *AC* and, therefore, $1 - x - y$ Mol. *AB*.

2. We take as components *AB*, *AC* and *CD*; p then represents: $1 - y$ Mol. *AB*, x Mol. *CD* and, therefore $y - x$ Mol. *AC*.

3. We take as components *AC*, *CD* and *BD*; the point p then lies outside the triangle having these substances as angles; it then represents $1 - y$ Mol. *BD*, $1 - x$ Mol. *AC* and, therefore, $x + y - 1$ Mol. *CD*; $x + y - 1$ is negative in this case.

4. If we take as components *AB*, *BD* *CD* p again lies outside the observed triangle; it then represents y Mol. *CD*, $1 - x$ Mol. *AB* and, therefore, $x - y$ Mol. *BD* which latter quantity is negative.

We may, therefore, assume in four ways that the phase p is constructed of three of the four substances; it is obvious that each of the four assumptions leads to the same composition. This may be explained also in the following manner.

If, for instance, we calculate the quantity A of this phase in the four ways described, we always get the same result: According to 1 the phase contains y Mol. AC and $1-x-y$ Mol. AB, therefore $1-x$ Mol. A; the same is found according to 2, 3 and 4.

We also find in each of the four cases that that phase contains $1-y$ Mol. B, y Mol. C and x Mol. D.

If we draw from p the perpendicular lines z and u these are also significant. For we find:

$$z=\frac{1}{2}(1-x-y)\sqrt{2} \quad \text{and} \quad u=\frac{1}{2}(y-x)\sqrt{2}.$$

For the composition of the phase p we may write according to 1.

x Mol. BD, y Mol. AC and $1-x-y$ Mol. AB.

As, however, between the four substances exists the relation

$$AB+CD=AC+BD$$

we may express the composition also in the four substances, for instance:

$x-n$ Mol. BD, $y-n$ Mol. AC, $1-x-y+n$ Mol. AB and n Mol. CD.

From this it follows that $1-x-y$ represents the number of Mols. AB minus the number of Mols. CD, while $y-x$ represents the number of Mols. AC minus the number of Mol. BD, Therefore:

$$z=\frac{1}{2}(\text{Mol. } AB-\text{Mol. } CD)\sqrt{2} \quad , \quad u=\frac{1}{2}(\text{Mol. } AC-\text{Mol. } BD)\sqrt{2}.$$

The half diagonal of the square is now $\frac{1}{2}\sqrt{2}$; if, however, the half diagonal is taken as 1 we have:

$$z=\text{Mol. } AB-\text{Mol. } CD \quad \text{and} \quad u=\text{Mol. } AC-\text{Mol. } BD.$$

The composition of the phase represented by point p may, therefore, be deduced in two ways.

1. From the situation of p in regard to one of the four triangles whose angles represent the solid substances. The length of the sides of the square is then called 1. We then obtain the composition expressed in those three substances which form the angles of the observed triangle.

2. From the situation of p in regard to the two diagonals of the square. The length of the half diagonals is then taken as 1.

If we now add a fourth component, this may be placed on an axis in the point O perpendicularly to the plane of the square; if on this we take a piece $OW = 1$, point W then represents the fourth component W. The different phases occurring in the system will then be represented by the points within the prism $W . AB . AC . CD . BD$.

As in the system now investigated the relation

$$Cu\,SO_4 + 2\,NH_4\,Cl = (NH_4)_2\,SO_4 + Cu\,Cl_2$$

takes place between the four salts we will, in the case of ammonium chloride, take the double molecule $(NH_4\,Cl)_2$ and not the single one. If we proceed along the circumference of the square in a constant direction the angles represent successively the components: $CuSO_4$, $CuCl_2$, $(NH_4Cl)_2$ and $(NH_4)_2SO_4$ the water will then be indicated by point W in space.

We may now project the different points in space on an arbitrary plane; for this we choose a projection on the square and then obtain something like what is represented in Fig. 2. As the drawing would become too large the diagonals have only been drawn as far as necessary; the sides and angles of the square have been omitted.

We will now consider first the different ternary systems.

1. The system: water, $CuSO_4$, $(NH_4)_2SO_4$.

In this system investigated by Miss W. C. DE BAAT three solid substances occur at 30° in equilibrium with the liquid, namely, $(NH_4)_2SO_4$, $Cu\,SO_4 . 5\,H_2O$ and $Cu\,SO_4 . (NH_4)_2\,SO_4 . 6\,H_2O$.

The isotherm therefore consists of three saturation lines, namely:

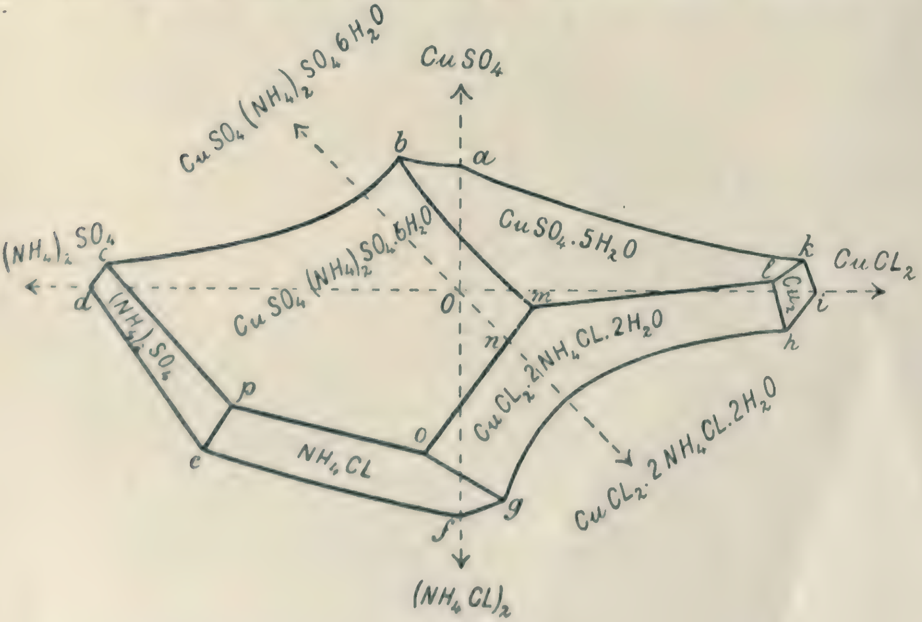

Fig. 2.

dc the saturation line of the $(NH_4)_2\ SO_4$
cb ,, ,, ,, ,, ,, $Cu\ SO_4 \,.\, (NH_4)_2\ SO_4 \,.\, 6\ H_2O$
ba ,, ,, ,, ,, ,, $Cu\ SO_4 \,.\, 5\ H_2O$.

If we unite the point O with the point representing the double salt $CuSO_4 \,.\, (NH_4)_2SO_4 \,.\, 6\ H_2O$ we intersect the saturation line of double salt the latter being, therefore, soluble in water without decomposition.

2. The system: water, $Cu\ SO_4$, $Cu\ Cl_2$.

Only two solid substances namely $CuSO_4 \,.\, 5H_2O$ and $CuCl_2 \,.\, 2\ H_2O$ occur in this system as solid phases by the side of liquid; point *k* is the solution saturated with both salts, *ki* is the saturation line of the $CuCl_2 \,.\, 2\ H_2O$, *ka* that of the $CuSO_4 \,.\, 5\ H_2O$.

3. The system: water, $CuCl_2$, NH_4Cl.

The isotherm of 30° has already been determined by Dr. P. Meerburg. As solid substances occur, by the side of liquid, $CuCl_2 \,.\, 2\ H_2O$, NH_4Cl and $CuCl_2 \,.\, 2\ NH_4Cl \,.\, 2\ H_2O$. The saturation line of the $CuCl_2 \,.\, 2\ H_2O$ is represented by *ih*, that of the $CuCl_2 \,.\, 2\ NH_4Cl \,.\, 2\ H_2O$ by *hg*, and that of the NH_4Cl by *fg*. The line uniting point *O* with the point representing the double salt intersects the saturation line of the double salt the latter being, therefore, soluble in water without decomposition.

4. The system: water, $(NH_4)_2SO_4$; NH_4Cl.

In this system only $(NH_4)_2SO_4$ and NH_4Cl occur as solid substances; the saturation line of the first salt is represented by *de*, that of the second by *ef*; *e* represents the solution saturated with both salts.

After this short review of the four ternary systems we can now discuss the quaternary system.

At 30° the following substances can occur as solid phases in coexistence with liquid:

$CuSO_4 \,.\, 5\ H_2O$, $CuCl_2 \,.\, 2\ H_2O$, $(NH_4)_2SO$, NH_4Cl, $CuSO_4 \,.\, (NH_4)_2SO_4 \,.\, 6\ H_2O$ and $CuCl_2 \,.\, 2\ NH_4Cl \,.\, 2\ H_2O$.

As the solutions, which in a quaternary system are saturated with solid matter are represented by a surface, there must be six saturation surfaces; their projections are indicated in the figure, namely:

abmlk is the saturation plane of the $CuSO_4 \,.\, 5H_2O$
iklh ,, ,, ,, ,, ,, ,, $CuCl_2 \,.\, 2H_2O$
fgope ,, ,, ,, ,, ,, ,, NH_4Cl
dcpe ,, ,, ,, ,, ,, ,, $(NH_4)_2SO_4$
hlmog ,, ,, ,, ,, ,, ,, $CuCl_2 \,.\, 2NH_4Cl \,.\, 2H_2O$
bmopc ,, ,, ,, ,, ,, ,, $CuSO_4 \,.\, (NH_4)_2SO_4 \,.\, 6H_2O$

In order to facilitate the survey, I have indicated on each of the saturation surfaces the solid substances with which the solutions are saturated; for the sake of brevity Cu_2 stands for $CuCl_2 . 2H_2O$.

The lines in which the surfaces intersect each other two by two represent the solutions saturated with two solid substances. They are the following:

ep, the saturation line of $(NH_4)_2SO_4 + NH_4Cl$
cp, „ „ „ „ $(NH_4)_2SO_4 + CuSO_4 . (NH_4)_2SO_4 . 6H_2O$
bm, „ „ „ „ $CuSO_4 . 5H_2O + CuSO_4 . (NH_4)_2SO_4 . 6H_2O$
lk, „ „ „ „ $CuSO_4 . 5H_2O + CuCl_2 . 2H_2O$
lh, „ „ „ „ $CuCl_2 . 2H_2O + CuCl_2 . 2NH_4Cl . 2H_2O$
og, „ „ „ „ $NH_4Cl + CuCl_2 . 2NH_4Cl . 2H_2O$
mo, „ „ „ „ $CuSO_4 . (NH_4)_2SO_4 . 6H_2O +$
$+ CuCl_2 . 2NH_4Cl . 2H_2O$
po, „ „ „ „ $CuSO_4 . (NH_4)_2SO_4 . 6H_2O + NH_4Cl$
lm „ „ „ „ $CuSO_4 . 5H_2O + CuCl_2 . 2NH_4Cl , 2H_2O$

The points in which the saturation lines meet three by three are the saturation points; they represent the solutions saturated with three solid substances. We have;

p, saturated with $CuSO_4 . (NH_4)_2SO_4 . 6H_2O + (NH_4)_2SO_4 + NH_4Cl$
o, „ „ $CuSO_4 . (NH_4)_2SO_4 . 6H_2O + CuCl_2 . 2NH_4Cl . 2H_2O +$
$+ NH_4Cl$
m, „ „ $CuSO_4 . (NH_4)_2SO_4 . 6H_2O + CuCl_2 . 2NH_4Cl . 2H_2O +$
$+ CuSO_4 . 5H_2O$
l, „ „ $CuCl_2 . 2NH_4Cl . 2H_2O + CuSO_4 . 5H_2O +$
$+ CuCl_2 . 2H_2O$

We can now see plainly from the figure the solid substances by the side of which a defined solid substance can exist in saturated solution. We notice that $CuSO_4 . (NH_4)_2SO_4 . 6H_2O$ can exist in coexistence with $(NH_4)_2SO_4$, NH_4Cl, $CuSO_4 . 5H_2O$ and $CuCl_2 . 2NH_4Cl . 2H_2O$ but not together with $CuCl_2 . 2H_2O$; $CuSO_4 . 5H_2O$ can exist by the side of $CuCl_2 . 2H_2O$, $CuCl_2 . 2NH_4Cl . 2H_2O$ and $CuSO_4 . (NH_4)_2SO_4 . 6H_2O$ but not together with $(NH_4)_2SO_4$ or NH_4Cl. It further appears that both double salts behave in regard to each other and to water as single substances; at 30° we may have a series of solutions saturated with $CuSO_4 . (NH_4)_2SO_4 . 6H_2O$, a series saturated with $CuCl_2 . 2NH_4Cl . 2H_2O$ and one solution saturated with both at the same time; the latter is represented by point *n*.

Many other conclusions may be drawn from the figure, but this I must leave to the reader.

Physiology. — "*Contributions to the Study of serumanaphylaxis*" (1st communication). By J. G. Sleeswijk, Foreign Member of the Pasteur Institute at Brussels. (Communicated by Prof. Spronck).

(Communicated in the meeting of January 30, 1909).

Of late the problem of anaphylaxis has attracted the particular attention of more than one investigator of immunity. On the one side the purpose is to answer the purely scientific question, how hypersensibility has to be explained, which in an organism may appear with respect to very different albuminous substances after such a material in some way or other has formerly been assimilated by the organism in question. But on the other hand the practical serumtherapy wishes to be delivered from the difficulties of the serumdisease, and tries to find means of preventing the dangers which, already with the first injection, but still oftener with an injection that is repeated not too soon, threaten the patient.

In the meantime the sphere of investigation has been examined in many a direction, the literature is increasing, but theory has still too frequently to complete what is wanting in a useful supply of facts. Therefore an extension of the latter is very desirable, if new points of view offer themselves there. This communication is to furnish a contribution to this. It contains in a few words some results of the first part of an investigation which was made in the Pasteur Institute at Brussels and which had the phenomenon of the serumanaphylaxis for its subject.

The literature will only be referred to, as far as this is strictly necessary to elucidate my explanation [1]).

It was Theobald Smith who had observed that guinea-pigs which had served for the titration of diphtheria-serum, and which accordingly had been treated previously with small quantities of diphtheriatoxine and antitoxic horse-serum, after a certain period of incubation had become extremely sensitive to a second injection of horse-serum, that they reacted thereupon as upon the administration of a strong poison and — in proportion to the dose — very often perished. Otto proved that with nothing but horse-serum (without toxine) this hypersensitiveness was also obtained, whilst Rosenau and Anderson proved that also with the aid of other sera such an anaphylactic state could be called into life, and that for each serum in a specific sense. Since that time the guinea-pig has become the fit test-animal for such investigations.

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[1]) For an ampler discussion about the present state of the problem I beg to refer to a critical study from my own hand, which is shortly to appear in the "Zeitschrift für Immunitätsforschung und experimentelle Therapie".

I have provisionally confined myself to the study of horse-serum, also because the knowledge of this in connection with the origin of our therapeutic sera has the most practical importance.

While a normal guinea-pig bears an intraperitoneal or subcutaneous injection of 5 cm^3 horse-serum without any perceptible symptom of disease, such an animal (of 250 to 300 grammes) mostly perishes however under typical symptoms of intoxication, when about 12 days before it has been treated with a small dose of the same serum (e. g. ± $^1/_{100}$ cm^3.). Instead of immunity (*pro*phylaxis), which usually follows on the administration of a larger dose, here a state of hypersusceptibility or *ana*phylaxis (Richet) has arisen. The horse-serum completely harmless in itself, plays in this case for the sensitized guinea-pig the part of a heavy poison. The first sensitizing injection must therefore have caused such changes in the organism as to change the second serum-injection into a toxic one.

This process of reaction no doubt belongs to the symptoms of immunity, and consequently it ought to be studied with the aid of the methods that the doctrine of immunity has procured. It was therefore a matter of course that the question was asked: Is in the process in question alexine fixed?

Otto[1]) answers this question in the negative, in my opinion wrongly. For repeated observation taught me that a sensitized guinea-pig, which reacts upon the second serum-administration with symptoms of intoxication some time after that injection produces a serum that is exceedingly poor in haemolytic alexine (sensitized red corpuscles serving as test-object). A short time (5—10 min.) after the toxic injection the alexic power of the pig-serum is still the same; after this it decreases gradually and rather rapidly, so that after $^1/_2$—1 hour it has become minimum. In this period the animal mostly dies. If it recovers, however, the alexine is also seen to increase again, so that 1$^1/_2$—2 hours after the injection it has returned again to the normal level or even higher. This course of things might be graphically represented by means of a curve. In a normal, not anaphylactic guinea-pig the alexine-quantity of the serum remains constant under the same experimental circumstances.

Now, if the blood is not examined at the right moment, or not at several moments during the stage of intoxication, the chances are that one is too early (when the alexine has not yet disappeared) or also too late (when it has recovered itself again). I presume that Otto has thus been led astray.

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[1]) Münch. med. Woch. 1907, no. 34.

I have still to add here that, if the second toxic injection is applied not in the abdomen or subcutaneously, but in the circulation — in consequence of which the symptoms of intoxication show themselves very soon and pass very quickly — these symptoms may already be present even before the alexine has disappeared from the serum of the animal. From this may be concluded that the symptoms of poisoning are not the consequence of the loss of alexine, but that these two are processes running parallel, independent of each other, but both having a common cause. And this can be no other but the reciprocal influence of the horse-serum administered (the antigen) and the reaction-products, specific for this, of the sensitized organism, arisen after and in consequence of the first injection of the alien serum.

This being settled, we continue asking ourselves: where are these reaction-products to be found — probably a particular kind of antibodies? Where do we meet with such materials as show a particular and specific affinity to horse-serum?

In order to answer this question, of course the first thing done was to examine the serum of sensitized guinea-pigs, but without any special result. For in not a single combination such serum gives a precipitate with horse-serum. Another possibility for the disappearance of the alexine from the serum of the intoxicated animals might still be found in the presence in their circulation of antialbuminoid sensibilisators of Gengou. But also these seem to be wanting; I have repeatedly been able to convince myself that anaphylactic serum, again in not a single combination with horse serum, is able to fix alexine. On the other hand I have been able to prove that the serum of the sensitized pigs reacts antialexically with respect to fresh horse-serum, and especially during the stage in which after the toxic injection the original alexine has disappeared from the circulation. Although I now reserve to myself the duty to revert to the meaning of this fact on a future occasion, yet it seems to me that this formation of antialexines (which we also meet with at the usual serum-immunity) does not bring us much nearer to the explanation of just the anaphylactic complex of symptoms.

But if not the fluids, it is perhaps the cells that can bring us a step onward? — I have applied to the erythrocytes of the guinea-pig, and it has appeared to me that washed normal pig-blood, brought in contact with horse-serum, whilst a sufficient quantity of physiological solution of sodiumchloride is present, is able to fix from the serum the substance that is toxic for sensitive animals.[1])

This procedure was already for another reason known in the immunity-literature, because in this way also the alexine from the horse-serum is fixed upon the blood of the guinea-pig.[2])

Serum treated thus has for anaphylactic animals lost its poisonousness, and this fact seems to me to open a new point of view. For it proves that there exists affinity between the toxic principle of horse-serum and cellular elements already of the normal pig-organism. The supposition does not seem to be too bold that also other elements of tissue or organs of the guinea-pig are subjectable to such a fixation, and that this affinity is still enhanced in the anaphylactized animal. The reaction between the horse-serum and the sensitive elements — especially those of the central nervous system — would then give rise to the action of the anaphylactic shock, whilst by the side of this the secondary fixation of the alexine would be the consequence of this reaction to be observed in the serum. Starting from these facts and considerations I continue my investigation in this direction.

In the meantime it is worth while to point out here that already some time ago v. Behring drew the attention to the paradoxical fact that a horse containing abundant diphtheria-antitoxines in its blood, can yet react upon a relatively small dose of toxine with symptoms of poisoning and even with death. Therefore v. Behring presumed the existence of an *histogenetic hypersensibility*, which hypothesis, in connection with what precedes, grows more probable.

To the many attemps made by different investigators with varying results, to deprive horse-serum of its toxicity by the help of physical or chemical means, I have tried to add another, which had a satisfactory result. I have namely submitted to dialysis horse-serum in so-called "Fischblasencondome". From this it appeared that the arising precipitation, dissolved in a physiological salt-solution, shows no trace of toxicity with respect to sensitized guinea-pigs, whilst the serum floating on the surface and free from salt (before the animal-experiment reduced to isotonical proportions), gradually loses its poisonousness during the process of dialysis.

Now the proof for the non-poisonousness just of the filtrate is not devoid of importance, because former investigations have shown that in dialysing antitoxical horse-serum the diphtheria-antitoxines (which are fixed to the soluble globulines) are to be found back quantitatively in the filtrate. Thus the way has been paved to obtain an antitoxical solution, at the same time free from anaphylactic by-actions, — which might be of great use to the serum-therapy. Erelong I hope to be able to give further information about this subject.

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[1]) Take for 1 vol. serum: $1^{1}/_{2}$ vol. blood and 2 vol. salt solution. — On simple dilution with salt-solution in the same proportions, the serum retains its toxicity.

[2]) See about the meaning of this phenomenon: Ehrlich and Sachs, Berl. Klin. Woch. 1902, no. 21 and Bordet and Gay, Annales Pasteur 1906.

Mathematics. — "*The types of bilinear ∞^r-complexes of M^n_{r-2} in Sp_r.*"

By Mr. Lucien Godeaux, at *Liège*. (Communicated by Prof. Schoute).

(Communicated in the meeting of January 30, 1909).

I have been recently [1]) investigating which were the essential characteristics of the most general type of the bilinear complex of conics in Sp_3; it is now my purpose to extend my work to the linear space Sp_r with r dimensions.

Let there be ∞^r varieties M^n_{r-2} with $r-2$ dimensions and of order n. Any one of these varieties is entirely situated in a linear space Sp_{r-1} of the fundamental space Sp_r. Let us say that these ∞^r varieties form a ∞^r-complex.

The characteristics of such a complex are:

1. The number μ of the M^n_{r-2} situated in a general Sp_{r-1} of Sp_r.

2. The number ν of the M^n_{r-2} passing through a fixed point and the Sp_{r-1} of which passes through a Sp_{r-2} containing the chosen fixed point.

The aim we have here in view is the determination of the essential properties of the most general ∞_r-complex L having the characteristics $\mu = 1$, $\nu = 1$.

Let us notice that all the varieties M^n_{r-2} of Sp_r are the sections by the Sp_{r-1} of the varieties V^n_{r-1} with $r-1$ dimensions and of order n of a linear system $\binom{n+r-1}{n}$ — 1-times infinite K.

The M^n_{r-2} of L are evidently situated on the V^n_{r-1} of an ∞^r-system K' contained in K.

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[1]) *Détermination des variétés de complexes bilinéaires de coniques.* Bull. de l'Acad. Roy. de Belgique 1908.

Theorem I. — *The* M^n_{r-2} *of* L *situated in the* Sp_{r-1} *passing through a fixed* Sp_{r-1} *generate a variety* V^{n+1}_{r-1} *of* $r-1$ *dimensions and of order* $n+1$.

Let d be a linear space Sp_{r-2}. Each Sp_{r-1} passing through d contains a M^n_{r-2}. Space d belongs to the variety generated by these M^n_{r-2}, for $\nu = 1$. We deduce from it the above theorem.

Theorem II. — *A* V^n_{r-1} *of the system* K' *contains generally but one* M^n_{r-2} *of* L. Let us suppose a V^n_{r-1} of K' containing two M^n_{r-2} of L and let us denote by α, β the Sp_{r-1} containing these two M^n_{r-2}. The M^n_{r-2} of which the Sp_{r-1} pass through the Sp_{r-2} common to α and β generate a V^{n+1}_{r-1} on which the points common to α, β and to the two M^n_{r-2} are multiple of order two.

From this ensues that through a point of the Sp_{r-2} common to α, β generally no M^n_{r-2} of L will pass of which the Sp_{r-1} would pass through this Sp_{r-2}, which is contrary to the hypothesis $\nu = 1$; hence the theorem.

Conclusion: We see that

1. An Sp_{r-1} contains a single M^n_{r-2} of L, thus to an Sp_{r-1} corresponds a single V^n_{r-1} of K'.

2. A V^n_{r-1} of K' contains a single M^n_{r-2} of L, thus to a V^n_{r-1} of K' corresponds a single Sp_{r-1}.

Hence:

A ∞^r*-complex of* M^n_{r-2} *with characteristics* $\mu = 1$, $\nu = 1$ *is the intersection of the elements of two varieties in birational correspondence; one of these varieties is composed of the* Sp_{r-1} *of the space, the other is a homaloid system of* V^n_{r-1} *r-times infinite.*

Liege, Oct. 1908.

Mathematics. — "*The plane curve of order* 4 *with* 2 *or* 3 *cusps and* 0 *or* 1 *nodes as a projection of the twisted curve of order* 4 *and of the* 1st *species.*" By Prof. H. DE VRIES.

(Communicated in the meeting of January 30 1909.)

1. If two quadratic cones are situated arbitrarily with respect to each other, they intersect each other in a twisted curve r^4 of order 4 and of the 1st species. If we suppose the plane τ to be brought through a point O of the nodal curve of the developable belonging to r^4 in which plane lie the two tangents of r^4 passing through O, then this plane must intersect the two cones according to conics k^2_1, k^2_2, touching each other in the points of contact O_1, O_2 of the two indicated tangents with r^4. We shall now suppose the first cone to be determined by the base-curve k^2_1 and the vertex R, the second by k^2_2 and the vertex S. The plane τ is a double tangential plane of r^4, so it must be a tangential plane of *one* of the four quadratic cones passing through r^4; i. e. in τ, and on the line O_1O_2, lies the vertex H of a third double projecting cone of r^4; and finally the vertex T of the fourth cone must then lie in the common polar plane of H with respect to the cones $[R]$ and $[S]$, and this plane must pass through O, because the double curve of the developable of r^4 consists of four plane curves of order four situated in the faces of the tetrahedron $R\,S\,T\,H$, and O, as a point of this double curve, must thus lie in *one* of those faces, namely in the polar plane $R\,S\,T$ of H, because the points O_1 and O_2, whose tangents intersect each other in O, lie on a straight line through H. The cone $[T]$ intersects τ in a conic k^2_3, likewise touching in O_1 and O_2 the lines OO_1, OO_2; the cone $[H]$ on the contrary has with τ only the line O_1O_2 counting double in common.

2. If we project r^4 out of O on an arbitrary plane π, then the projection is a plane curve k^4 with two cusps in the points of intersection of this plane with OO_1, OO_2; it is convenient to take for this plane of projection the polar plane of O with respect to the cone $[H]$, because then O_1, O_2, together with two other important points — of which we shall soon hear more — coïncide with their projections; the cuspidal tangents are nothing but the traces of the osculating planes of r^4 in O_1, O_2 with π.

The plane π intersects the cone $[H]$ in two generatrices; one is O_1O_2, the other intersects r^4 in two points D_1, D_2 coïnciding with their central projections on π, and in which k^4 touches the line D_1D_2, because the plane through this line and O is a tangential plane of $[H]$; so D_1D_2 is the double tangent of k^4, and H is the point of intersection of this double tangent with the connecting line O_1O_2 of the cusps [1]).

Each generatrix of $[H]$ contains two points of r^4, lying harmonically with respect to the point H and the point of intersection with the polar plane RST of H; so if we call h the line of intersection of this plane with π, it ensues immediately that *each line of π through H contains four points of k^4, lying harmonically in two pairs with respect to H and h*; each pair originates from two points on a generatrix of $[H]$.

If we consider O_1, O_2, D_1, D_2 as base-points of a pencil of conics, then for each curve of this pencil H is the pole of h; each curve containing the cusps and the points of contact of the double tangent of k^4, it cuts this curve in two more points P_1, P_2, whose connecting line passes through H. These pairs of points determine on k^4 a fundamental involution in such a way that on each ray through H lie two pairs, originating from the two pairs of points of r^4 on two generatrices of $[H]$ situated with O in one plane; the conics of the pencil are thus arranged by the rays out of H in pairs of a quadratic involution, whose double elements correspond to O_1O_2 and the double tangent d; the former consists of the conic of the pencil touching in O_1 and O_2 the cuspidal tangents, a curve which together with h forms the first polar curve of H with respect to k^4; the second must break up into the lines O_1O_2 and d, because this conic must touch the line d in D_1 and D_2. By the pencil (H) and the pencil of conics $(O_1,O_2,\ D_1,D_2)$ paired involutorily conjugated to it k^4 is generated as the locus of the points of intersection of corresponding elements, where besides k^4 also the line d appears. [2]).

However, k^4 can be generated in still another way. Let us imagine through O_1O_2 instead of π another plane; this will intersect r^4 besides in O_1,O_2 in two more points P_1, P_2, whose connecting line passes through H and is divided harmonically by these three points and the plane $R\,S\,T$; so the central projections P'_1, P'_2 are situated likewise on a line through H, and lie harmonically with respect to H and h. Let us now consider the pencil of conics $(O_1,O_2,\ P'_1,\ P'_2)$. The different conics of this pencil are likewise involutorily paired by the pencil (H); the branchrays are again O_1O_2 and d, the double conics conjugated to them are the conic of the pencil touching in

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[1]) See the paper of Prof. JAN DE VRIES (Proceedings of Amsterdam of Dec. 1908 p. 499): "On bicuspidal curves of order four".

[2]) J. DE VRIES, l. c. p. 500.

O_1, O_2 the cuspidal tangents and the one passing through D_1, D_2. The locus of the points of intersection of corresponding elements consists of k^4 and the line $P'_1 P'_2$.

We can finally allow P'_1, P'_2 to coïncide with the cusps, we can thus consider all the conics touching the cuspidal tangents in O_1, O_2; these too are paired involutorily by the pencil (H) whilst the branch-rays are again represented by d and $O_1 O_2$; to d is again conjugated the polar conic of H, to $O_1 O_2$ a conic having in each of the two cusps four coïnciding points with k^4 in common; so it can be nothing but the line $O_1 O_2$ counted double. As the locus of the points of intersection of corresponding elements of both pencils appears this time besides k^4 still the line $O_1 O_2$.

3. Among the planes of the pencil $(O_1 O_2)$ are of special importance those containing the cone-vertices R, S, or T; the former e.g. is the polar plane of O with respect to the cone $[R]$ and contains therefore the two generatrices RO_1, RO_2. Each of these cuts r^4 in one point more, e.g. R_1 and R_2; the tangential planes along these generatrices to $[R]$ pass through O however; and from this ensues that the central projections of RO_1 and RO_2, cutting each other in the projection R' of R lying on h, must touch k^4 at the points R'_1, R'_2. We can, however, also bring through O two tangential planes to the cones $[S]$ and $[T]$, so: *out of each of the two cusps three tangents can be drawn to* k^4, *the traces of the tangential planes through* O *to the cones* $[R]$, $[S]$, $[T]$; *these tangents intersect each other in pairs in three points* R', S', T' *of* h[1]) (this also follows from the harmonic position of the whole figure with respect to H and h), *the projections of the three cone-vertices* R, S, T.

Remark. If we take for k_1^2, k_2^2 (see § 1) two concentric circles, and if we then project the figure in space on a plane π (§ 2) which is parallel to τ, the oval of DESCARTES is generated and R', S', T' pass into the foci.

The twisted curve r^4 can be generated in six different ways as intersection of two of the four cones; let us take in particular $[R]$ and $[H]$. If we make to pass through the line RH two planes μ_1, μ_2, harmonically separated by the planes RHS and RHT, the points of the two quadruples of points lying in these planes are situated two by two on four straight lines through each of the four cone-vertices; we now take for μ_1 the plane passing through the points O_1, O_2, R_1, R_2, and we shall call the four points in the other plane S_1, S_2, T_1, T_2. The latter four points lie thus with the former on four straight lines through S and on four others through T; let us now suppose e. g. that O_1S_1 passes through S. The tangential plane along the line SS_1O_1 to the cone $[S]$ has then as trace with τ the tangent in O_1 to k_2^2, i. e. the line OO_1, and from this ensues that the four points S_1, S_2, T_1, T_2 are nothing but the points of contact of the tangential planes through O of the cones $[S]$ and $[T]$ with r^4; however, we know now that these four points lie on two lines through R, so *in projection the points of contact* S'_1, S'_2, T'_1, T'_2 *of the tangents out of the cusps not passing through* R' *lie on two straight lines through* R', *namely* S'_1 *with* T'_2, *and* S'_2 *with* T'_1.[1] That they lie also on two lines through H follows moreover again from the harmonic position with respect to H and h.

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[1]) J. DE VRIES, l. c. p. 501.

The polar plane of R with respect to the remaining three cones is simply the plane STH; it intersects the plane RST in the line ST (whose central projection falls on h), and the two lines of intersection with μ_1 and μ_2 lying in this plane in two points R^*, R^{**}, lying on ST, and situated harmonically with respect to S and T; R^* is then the point of intersection of O_1R_2, O_2R_1, R^{**} that of S_1T_1 and S_2T_2. If we transfer these results to the projection, we find: *of the complete quadrangle* $O_1O_2R'_1R'_2$ *two of the diagonal points are* R', $R^{*\prime}$ (*the third is* H), *and of the quadrangle* $S'_1T'_2T'_1S'_2$ *likewise* R', $R^{**\prime}$; *the points* $R^{*\prime}$ *and* $R^{**\prime}$ *lie harmonically with respect to* S' *and* T'. A similar property of the same points holds if we combine S'_1, S'_2 with the cusps and then regard the other four points; or finally if we couple T'_1, T'_2 to O_1, O_2 and join the other four to a complete quadrangle. And finally all six points $R'_1 \dots T'_2$ lie on a conic in consequence of the harmonic position with respect to h and H, whilst the points of intersection not lying on h of the six tangents out of the cusps lie likewise on a conic and at the same time in pairs on three straight lines through H.

4. Besides the group of 8 points just considered consisting of the two cusps and the points of contact of the six tangents passing through these points, there lie on k^4 still an infinite number of other suchlike groups which have with respect to R', S', T', H the same properties. Let us for instance suppose that the plane μ_1 (§ 3) is still passing through RH but for the rest arbitrary, and let us suppose μ_2 again as harmonically conjugate to μ_1 with respect to HRS, HRT, then on r^4 a new group of 8 points is generated

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[1] J. de Vries, l. c. p. 498.

lying in pairs on four lines through each of the 4 vertices, and whose central projections thus possess the same property with respect to the points R', S', T', H. If we divide the 8 projections into two quadruples, in such a way that one belongs to the four points of μ_1, the other to those of μ_2, then the two quadruples form two complete quadrangles with the common diagonal points R' and H, whilst the others, $R^{*\prime}$ and $R^{**\prime}$, lie harmonically with respect to S' and T'; *the pairs of points* $R^{*\prime}$, $R^{**\prime}$ *on* h *form therefore a quadratic involution with the double points* S', T'. Similair properties hold for the two other possible divisions of the group of 8 points into two quadruples, namely with respect to the points S and T.

A special group of 8 points is found by choosing for the two planes μ the tangential planes through the line RH to the cone $[H]$, for these are likewise harmonically separated by HRS, HRT, but they furnish instead of 8 points 4 pairs of coïnciding points of r^4, namely the points of contact of the 4 tangents out of R to r^4. These points of contact lie in the polar plane ϱ (§ 3) of R and on two generatrices of the cone $[S]$, and likewise on two of the cone $[T]$; the tangents themselves pass in projection into the four tangents of k^4 through R' not passing through the cusps, so: *the points of contact of the four tangents of* k^4 *through* R' *not passing through the cusps are the vertices of a complete quadrangle whose diagonal-points are the points* S' T', H; the corresponding points $R^{*\prime}$, $R^{**\prime}$ are the points of intersection of the two sides of that quadrangle passing through H with h.

Another special group of 8 points is generated if we choose for the planes μ the tangential planes through RH to the cone $[R]$; we then find the four points of r^4 in the plane RST, and therefore in projection the points of intersection of r^4 with h, whose tangents indeed pass through H, in consequence of the harmonic position of k^4 with respect to h and H.

5. A group of 8 points of k^4 must be determined by *one* of these points; for the connecting line of this point with O intersects r^4 in *one* point, which determines with the line HR the plane μ_1; and by μ_1 at the same time μ_2 is determined. Planimetrically we can deduce out of *one* point of a group the other ones with the aid of the following property. The cone $[R]$ intersects the plane $\varrho = STH$ in a conic r^2, and we find that r^4 lies harmonically with respect to this and the point R, in that sense that the two points of r^4 on a generatrix of $[R]$ are always harmonically separated by R and the point of intersection with r^2; in particular r^2 contains

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the four points of intersection of r^4 with ϱ, whose tangents pass through R, and also the points harmonically conjugate to R with respect to the pairs O_1, R_1 and O_2, R_2 lying in the polar plane $O_1 O_2 R$ of O with respect to the cone $[R]$.

By passing to the projection we find out of this the following property of k^4: *through the points of contact of the four tangents out of R' not passing through the cusps, a conic r'^2 can be brought touching the two tangents which do pass through the cusps in the points harmonically conjugate to R' with respect to the cusps and the corresponding points of contact; k^4 now lies harmonically with respect to R' and r'^2 in such a sense that the four points of intersection of k^4 with an arbitrary ray through R' arrange themselves into two pairs, each lying harmonically with R' and one of the points of intersection of that ray with r'^2.*

Of course also the points S' and T' possess such a conic, but the point H likewise, namely the line h counted double; for, the polar plane of H with respect to r^4 is the plane $R\,S\,T$, and the section with the cone $[H]$ lying in this plane is projected out of O into the line h to be counted double.

With the aid of the conic r'^2 it is easy to deduce out of *one* point of a group the seven other ones. If point 1 is taken arbitrarily, we find four others by the harmonic position of k^4 with respect to the points R', S', T', H and the corresponding conics; on the line $R'1$ e.g. are lying besides 1 still 3 points of k^4, but among these is only *one* forming with 1, R', and *one* of the points of intersection of $R'1$ with r'^2 a harmonic group. The three then still missing points we find by simply combining in proper fashion the already found one with R', S', T', or H.

Just as in § 2 by rays out of H now, too, a fundamental involution is generated on k^4 by those out of R' (or S', or T') in such a manner that on each ray lie two pairs, originating from the two pairs of points of r^4 on two generatrices of the cone $[R]$ lying with O in one plane; each pair is harmonically separated by R' and *one* of the two points of intersection of the indicated ray with r'^2. If now in two points of r^4 lying on a straight line through R we draw tangents, then these intersect each other in a point of the plane STH, and the locus of this point of intersection is a plane curve of order four, double curve of the developable of r^4, with double points in S, T, H and having with r^4 the four points of intersection of r^4 with the plane STH in common.

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[1]. J. DE VRIES, l. c. p. 498.

Let us consider in particular the points O_1, R_1 (§ 3), lying on a straight line through R, and let us remember that the tangent in O_1 to r^4 passes through O; we shall then find on OO_1 a point of the double curve of order four, whilst the tangent in that point is the line of intersection of the osculating planes of r^4 in O_1 and R_1; that one of O_1 passes through O and furnishes in projection the cuspidal tangent in O_1 to k^4; so the central projection of the double curve will contain the cusps of k^4, and will touch the cuspidal tangents here.

So, summing up we find: *the point of intersection of the tangents to* k^4 *in two conjugate points of the involution generated by the pencil* (R') *generates a curve of order four with double points in* S', T', H, *situated harmonically with respect to* h *and* H *and having with* k^4 *in common the tangential points of the four tangents out of* R' *not passing through the cusps and likewise the cusps and the tangents in these.*

The new curve of order four cuts k^4 besides in the cusps (counting together for six points of intersection, and the tangential points of the four tangents out of R' not passing through the cusps, in six points more, of course again situated two by two harmonically with respect to h and H; now these six points lie twice with two of the four above mentioned points of contact (those namely whose connecting line passes through H) on a conic. For, the conic through two of those points of contact touching in O_1 and O_2 the cuspidal tangents of k^4, contains $2 \times 3 + 2 = 8$ points of intersection of the two curves of order four; so the other eight must also lie on a conic.

Also to the points S' and T'' belongs such a locus of order four; as to the point H we can observe that in space the locus belonging to H lies in the plane $R\,S\,T$ and passes through O, so it passes by central projection into the line h counted three times, because each line passing through O and lying in the plane $R\,S\,T$ intersects the curve besides in O in three more points; indeed, through each point of h pass three pairs of tangents to k^4, whose chords of contact pass through H. The central projection of O itself however is undetermined, and so h is covered with points for the fourth time; the locus belonging to H consists thus of the line h counted four times.

Remark. The properties found in this § hold in a somewhat more general form also for k^4 with two nodes, because they have been simply arrived at by centrally projecting the complete figure of the tetrahedron of Poncelet; the points R', S', T'', H have then however not such a simple position as for the bicuspidal k^4.

6. If we bring the vertex S of the cone $[S]$ on the surface of $[R]$, then T coïncides with S, whilst the point $S = T$ becomes a node of r^4; so k^4 possesses besides the two cusps a node and in this point S' and T' lie united. Out of each cusp only one tangent more can be drawn to k^4, and these two tangents intersect each other in the point R' lying on h. Through this point pass two more tangents to k^4, the projections of the two generatrices of the cone $[R]$ touching r^4. The points of contact of these two tangents with r^4 lie in the plane ϱ (§ 4), the common polar plane of R with respect to the cones $[S]$ and $[H]$, and so on the conic r^2 which has this plane in common with the cone $[R]$. This conic contains the vertex S; *so now k^4 is harmonically situated with respect to the point R' and the conic r'^2 passing through the double point and the points of contact of the two tangents out of R' not passing through the cusps, and touching the tangents out of R' which do pass through the cusps in the harmonically conjugated points of R' with respect to the cusps and the points of contact.*

If we bring through the line HR an arbitrary plane μ_1 (see § 4), then the harmonically conjugate μ_2 always coïncides with the tangential plane HRS to $[H]$, which plane contains no other point of r^4 than the node; of each group considered in § 4 of 8 points there are four coïnciding in the node, whilst the four remaining ones form a complete quadrangle with the diagonal points R, H, R^*. The tangents to r^4 in two points on a straight line through R intersect each other in ϱ and the locus of this point of intersection is a plane k^3 containing the node of r^4, having in this point a cusp (with cuspidal tangent in the plane RST), passing through H and having with r^4 two points in common, whose tangents pass through R. So if we pass to the central projection of r^4, we find that *by the rays of the pencil (R') on k^4 again a quadratic involution is generated in such a way that the two points of each pair form with R' and one of the two points of intersection of the ray under discussion with r'^2 a harmonic group; the point of intersection of the tangents in the points of a pair moves along a cubic curve lying harmonically with respect to h and H, containing the cusps of k^4 and touching here the cuspidal tangents, passing through the points of contact of the two tangents out of R' not passing through the cusps, passing through H and having in the node of k^4 a cusp with cuspidal tangent h.*

The cusps, the point of contact of the two tangents out of R' and the node represent all the twelve points of intersection of the cubic curve with k^4.

7. If, still imagining that the cone-vertices S and T are united in a point of the surface of $[H]$, we suppose the cone $[S]$ to be such that it touches the tangential plane in S to $[H]$, then r^4 gets a cusp in S and R coïncides with S and T, so that through r^4 pass but two quadratic cones; the plane $R\,S\,T$ remains determined, as the polar plane of H with respect to the cone $[R] = [S] = [T]$, and in this plane lies the tangent in the cusp R. The central projection now becomes a k^4 with three cusps, and the cuspidal tangent in R' is the line h. The double tangent through H remains determined as a trace of the plane of projection with the second tangential plane through O to $[H]$; however, as is easy to prove from the stereometric diagram, the points of contact must necessarily be imaginary.

As k^4 is situated harmonically with respect to h and H, the tangents in the cusps O_1, O_2 must intersect each other on h; however, h is the tangent in the cusp R': *so the three cuspidal tangents pass through one point.*

The point H forms with the cusps O_1, O_2, and the point of intersection of the line $O_1 O_2$ with h a harmonic group; but now the same must hold for the two other sides of the $\triangle O_1 O_2 R'$ of the cusps; *the double tangent d is therefore the so-called harmonical line of the points of intersection of the three cuspidal tangents with respect to the triangle of the three cusps; and the points of contact of the double tangent are the nodes of the elliptic involution on d, of which the points of intersection of d with the sides of that triangle and with the cuspidal tangents in the opposite vertices are three pairs. With respect to each cuspidal tangent and the point of intersection of the opposite side of the triangle with it the curve lies harmonically with itself.*

Zoology. — "*On Ptilocodium repens a new Gymnoblastic Hydroid epizoic on a Pennatulid.*" By Miss WINIFRED E. COWARD B.Sc. Victoria University of Manchester. (Communicated by Prof. MAX WEBER).

(Communicated in the meeting of January 30, 1909.)

Order. Gymnoblastea — Anthomedusae.
Family. Ptilocodiidae. fam. nov.
Ptilocodium repens: gen. nov., sp. nov.
"Siboga" Expedition Stat. 289. 9° 0,3 S. 126° 24,5 E. 112 metres.

Among the Pennatulids sent to Professor HICKSON from the Siboga

Expedition were two specimens of Ptilosarcus sinuosus (Gray)., and growing over the tips of the leaves of them a small epizoic hydroid was discovered. To a description of this new hydroid, the present paper is devoted.

The occurrence of an epizoite on a Pennatulid is in itself an interesting fact as the Pennatulids have usually been regarded as being peculiarly free from any such growths. Only two specimens of Ptilosarcus were received from the Expedition and the hydroid occurs on both of them. The other Pennatulids of the collection have been carefully looked over, but on none of them has an extraneous growth of any kind been found.

Ptilosarcus belongs to the Pennatuleae, the section of Pennatulids which are distinctly bilaterally symmetrical and have the autozooids in rows, with their body walls fused to form leaves.

Along the free edges of the leaves of the given specimens of Ptilosarcus, the hydroid Ptilocodium grows (fig. 1). It is quite visible to the naked eye, though in a cursory glance over the leaves of the Pennatulid, it probably would not be noticed. The hydroid affects the free edges of all the leaves of the Pennatulid, even those at the free extremity. It is suggestive that it does not spread over the rachis of the Pennatulid nor even over the main surfaces of the leaves, but grows only over the oral ends of the autozooids.

The hydroid is devoid of any kind of skeleton and spreads over the distal parts of the autozooids composing the leaves of the Ptilosarcus (figs. 2, 3). The colony grows by means of spreading stolons. These stolons run singly over the spicular projections of the autozooids and along their tentacles; (figs. 2, 3, 4) but over the part immediately below this, they branch and closely anastomose forming a more or less continuous sheet of basal coenosarc.

The hydroid exhibits the phenomenon of dimorphism, the gasterozooids and dactylozooids being quite distinct. The zooids are sessile, arising directly from the stolon or basal coenosarc as the case may be.

The dactylozooids arise at very short intervals along the stolon and are far more numerous than the gasterozooids. Gonozooids occur at frequent intervals. They are much fewer in number than the

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Note by Professor Hickson. The hydroid described in this paper was found on the only two specimens of Ptilosarcus in the Siboga collection. As they appeared to be of very great interest, and I could not part with the Pennatulids which are themselves under investigation, I considered it to be advisable, in the interests of science, that a description of them should be prepared in my laboratory without undue delay. I wish to express my hearty thanks to M. Billard, to whom the description of the Hydroidea of the Expedition has been entrusted for kindly giving his sanction to the publication of this paper independently of his memoir.

gasterozooids but in every case the gonozooid arises, not from the stolon but from the base of a gasterozooid (fig. 7) in close proximity to the stolon or basal coenosarc.

Stolon.

The stolons are tubular in structure (fig. 3). Their walls consist of superficial ectoderm and a lining of endoderm separated by a structureless lamella, the mesogloea. The ectoderm exhibits no traces of a perisarc. It possesses a few scattered nematocysts of the smaller kind .008 mm. × .005 mm. (vide infra).

Basal Coenosarc.

The basal coenosarc is formed by the anastomosing of stolons running over the parts of the autozooids immediately behind the tentacles. When two stolons run together or cross, the ectoderm of the dividing walls disappears so that the upper ectoderm of one stolon becomes continuous with the upper ectoderm of the other and the lower ectoderm of the one becomes continuous with the lower ectoderm of the other. Thus the basal coenosarc of the hydroid consists of superficial ectoderm and lower ectoderm separated by endodermal tubes (fig. 5). The structure arrived at is thus the same as in the coenosarc of Hydractinia except that Ptilocodium has no chitinous skeleton.

Nematocysts.

The hydroid possesses two sets of nematocysts. The larger kind is found in the dactylozooids. Here the nematocysts are oval in shape and measure .017 mm. × .008 mm. The smaller kind occurs in the ectoderm of the basal coenosarc and of the gonozooid, the size of these nematocysts being .008 mm. × .005 mm.

Gasterozooids.

Gasterozooids occur at frequent intervals on the basal coenosarc and are sessile (fig. 7). They vary in size from .213 mm. high and .106 mm. broad, to .373 mm. high and .026 mm. broad. They are much reduced in structure. There are no traces of tentacles. The zooid is simple and sac-like; the mouth is a simple pore leading from the exterior into the cavity of the zooid. The gasterozooids show no nematocysts. The endoderm cells near the mouth of the gasterozooids are comparatively short whilst those lining the remainder of the gastral cavity are long and narrow. The material is not sufficiently well preserved to make out clearly the histological structure of the cells but it seems probable that the digestive functions are preformed by the long, narrow cells of the basal half of the gasterozooids.

Dactylozooids.

The dactylozooids are very numerous compared with the gasterozooids. They occur at irregular intervals; there seems to be no definite relation, as regards arrangement on the basal coenosarc, between the dactylozooids and gasterozooids such as we find in Millepora or Stylaster.

The dactylozooids are short and broad and each bears four capitate tentacles crowded with large nematocysts (fig. 6). The zooids do not vary much in size, the average size being .186 mm. × .106 mm. The smallest zooids measure .106 mm. × .053 mm. The capitate tentacles are .038 mm. in length and .033 mm. broad. The nematocysts of the tentacles are of the larger of the two kinds possessed by the hydroid and measure .017 mm. × .008 mm. The ectoderm of the remainder of the zooids shews no nematocysts. The endoderm of the dactylozooids and tentacles is solid and scalariform, there being no trace of a cavity or oral opening. (fig. 6). Judging from the preserved specimens the dactylozooids seem little, if at all, contractile.

Gonozooids.

The gonophores which are adelocodonic, arise in each case, as before described, from the base of a gasterozooid. Thus the base of a gasterozooid functions as a blastostyle (fig. 7).

The gonozooids vary little in size, the average being .373 mm. × .186 mm. They are considerably reduced in structure, having the form of closed sporosacs. All the gonophores on the two specimens received are female. The ova are borne between the ectoderm and endoderm of the manubrium and have a diameter of .017 mm. They are practically all of the same size but it cannot be said whether or not they are ripe.

The superficial ectoderm of the gonozooid and the ectoderm lining the cavity corresponding to the sub-umbrella cavity of a medusa, are separated by an endoderm lamella, which shows traces of radial canals (figs. 7 and 8). There is no velum and there are no sense organs and only traces of four rudimentary tentacles. Nematocysts of the smaller kind occur in the superficial ectoderm of the gonozooids.

The Relation between the Hydroid and Ptilosarcus.

The specimens of Ptilosarcus sinuosus on which the hydroid is growing seem practically unaffected by it. The autozooids are well developed, showing no signs of degeneration.

The hydroid spreads only over the oral ends of the autozooids, that is, it keeps near the tentacles of the same, and does not run far over the leaves of the Pennatulid. Correlated with this is the fact that the gasterozooids of the hydroid are devoid of organs for catching food. These facts at once suggest that the Ptilosarcus benefits the hydroid by helping it to secure food.

On the other hand, on looking at a preparation of the hydroid, one is struck by the great number of dactylozooids which are so well provided with large nematocysts. Such a protection as these are capable of affording is probably more than is required by the small hydroid. The large projecting spicules of the autozooids of the Pennatulid also, would protect the hydroid. Therefore I would suggest that the Ptilocodium is of use to the Pennatulid in the warding off of enemies and in stinging prey by means of its batteries of large nematocysts and that the Ptilosarcus by means of its projecting spicules, protects the Hydroid. Thus the Ptilosarcus and Ptilocodium are mutually benefited.

Systematic position.

Ptilocodium seems to have some affinities with Hydractinia, Podocoryne and Millepora, as shewn by the sheet-like, encrusting basal coenosarc from which the zooids arise independently; but even in this character Ptilocodium stands alone in having no chitinous or calcareous skeleton to protect it.

In other respects Ptilocodium is unique. The dimorphism of Ptilocodium is quite distinct from that of Hydractinia and Millepora, and probably originated independently. In the first place, the gasterozooids of Ptilocodium are extremely unlike those of Hydractinia and Millepora. They are short, sessile, sac-like structures, without tentacles. Those of Hydractinia are long, filiform structures, provided with a crown of tentacles. The gasterozooids of Millepora are also much longer than broad, not at all sac-like in form, and are provided with knob-like tentacles.

The dactylozooids, also, are very different in structure, in the three genera. Those of Ptilocodium are short and broad, and are furnished with four characteristic capitate tentacles. The endoderm of the body of the zooid and of the tentacles is solid and scalariform, giving the dactylozooids a marked appearance. The dactylozooids of Hydractinia are long and slender and very muscular so that they are capable of coiling and uncoiling themselves. They have also a central cavity and according to Miss COLCUTT[1]) are provided with a terminal mouth. The dactylozooids of Millepora are very similar to those of Hydractinia. In possessing a solid scalariform endoderm, Ptilocodium resembles the Stylasterina. All the genera,except one, of this group, have the endoderm of the dactylozooids solid.

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[1]) Quart. Journ. Micro. Sci. No. 157, 1897.

In all other points except the dimorphism, however, Ptilocodium differs from the Stylasterina, and on the importance of dimorphism as indicating close relationship too much stress should not be laid. The old group Hydrocorallinae affords an illustration of the result of laying too much stress on this factor. In this group, the Milleporina and the Stylasterina were formerly united, but it has since been pointed out that differences of more importance necessitate their being classed as separate orders.

The next point to consider in discussing the relationship between Ptilocodium, Hydractinia and Millepora, is that of the gonophores. Ptilocodium resembles Hydractinia in having adelocodonic gonophores but differs from it in having the gonophores arising from the base of the ordinary gasterozooid and not from a specialised individual or blastostyle. In Millepora there is no blastostyle and the medusae arise independently of the gasterozooids, from the surface of the colony.

In Perigonimus, which, in the important respect of the structure of the basal coenosarc does not closely resemble Ptilocodium or Hydractinia, the gonophores arise from the hydrocaulus bearing the gasterozooid or from the hydrorhiza. This case may therefore be taken as an indication that too much stress must not be placed on the position of origin of the gonophore in the colony.

Ptilocodium stands quite apart from other genera of Hydroids with epizoic habits.

The epizoic Hydroid Stylactis minoi described by ALCOCK [1]) was found on the fish Minous inermis, but differs considerably from Ptilocodium. It has hydranths crowned with numerous tentacles rising from the hydrorhiza. It is not provided with dactylozooids of any kind and its gonophores are in the form of sporosacs arising from specialised individuals which bear tentacles.

Ptilocodium also differs considerably from Hydrichthys mirus, a Hydroid described by FEWKES [2]) as epizoic on the fish Seriola zonata. This hydroid exhibits structures of two kinds arising from the basal plate. In the first place there are long, filiform hydranths, which are looked upon as degenerate gasterozooids and secondly clusters of botryoidal gonosomes. Dactylozooids do not occur.

Ptilocodium has obviously no affinities with the hydroid Nudiclava described by LLOYD [3]), nor with Moerisia lyonsi, a Hydromedusan from Lake Qurun, described by C. L BOULENGER [4]).

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[1]) ALCOCK A. Ann. & Mag. Nat. Hist. 1892 vol. X p. 207.

[2]) FEWKES. Bull. Mus. Comp. Zoöl. vol. XIII p. 224.

[3]) LLOYD R. E. Records of Indian Museum. Vol. I. Part IV.

[4]) BOULENGER C. L. Quart. Journ. Micros. Sci. Vol. lii Jan. 1908.

In consequence of these considerations the only course to adopt is to regard Ptilocodium as the representative of a new family.

The above piece of work was undertaken at the suggestion of Professor Hickson, to whom I wish to express my sincere thanks for his most generous advice and assistance.

EXPLANATION OF PLATE.

aut — autozooid of Ptilosarcus.
bas coen. — basal coenosarc of hydroid.
dact. — dactylozooid of hydroid.
ect. — ectoderm.
ect. man — ectoderm of manubrium.
end. — endoderm.
end. can. — endoderm canal.
end. lam. — endoderm lamella.
end. man — endoderm of manubrium.
gast. — gasterozooid of hydroid.
gon. — gonozooid of hydroid.
mes. — mesentery of autozooid of Ptilosarcus.
nem. — nematocyst.
ov. — ovum of Ptilosarcus.
rad. can. — radial canal.
spic. — spicule.
stol. — growing tip of stolon.
sub. ect. — ectoderm lining the cavity corresponding to the subumbrella cavity of a medusa.
sup. ect. — superficial ectoderm of gonophore.
tent. — tentacle.
t. p. — tentacles of Pennatulid.

Fig. 1. External view of parts of two successive leaves of the Pennatulid, shewing the extent of the surface of the leaves, affected by the hydroid.

Fig. 2. Drawing of a microscope preparation of part of the free edge of a leaf of Ptilosarcus, shewing the hydroid running out over the spicular projections of the autozooids × 20.

Fig. 3. Drawing of a preparation similar to 2. × 68.

Fig 4. Longitudinal section of a Pennatulid leaf shewing the hydroid growing over the free edges of the leaf.

Fig. 5. Vertical section of basal coenosarc of the hydroid shewing superficial and lower ectoderms, and endoderm canals.

Fig. 6. Optical section of dactylozooid of hydroid shewing solid endoderm, and the characteristic four tentacles.

Fig. 7. Longitudinal section of gonozooid arising from base of gasterozooid.

Fig. 8. Transverse section of gonozooid.

Zoologie. — "*On the spinispirae of Spirastrella bistellata* (*O. S.*) *Ldfd.*" By Dr. G. C. J. Vosmaer, Professor at the University of Leiden.

(Communicated in the meeting of January 30, 1909).

Some years ago (1902) I drew attention to the fact that there is confusion with regard to the terminology of certain sponge-spicules, and tried to clear this up. I arrived then at the conclusion that the spicules, which are generally called "spirasters", far from being a sort of "asters", i. e. polyaxon spicula, ought really to be considered as monaxons, the axis of which is a helix screw. I proposed for that kind of monaxons the term *spiraxon* (l.c. p. 105 and 112). In order to avoid further confusion I called the spined forms: *spinispirae.* I had some doubts about the supposition of some authors, that transitions between true asters and spinispirae really existed, because I never found them and failed to find any proof in literature (l.c. p. 105). On the one hand authors make a certain distinction between true asters (euasters) and "spirasters", but on the other hand consider both forms as belonging to the same group. Thus Topsent (1900 p. 21) distinguishes the genera *Hymedesmia* and *Spirastrella* on account of the fact, that the microscleres of the former genus are "euasters", of the latter "spirasters". It is generally accepted that the microscleres of *Hymedesmia stellata* are euasters; but with regard to *H. bistellata* there is diversity of opinion and confusion. I believe this to be due to an erroneous conception of the spicules under consideration. Although I was convinced for myself, that these spicules were by no means (polyaxon) asters, but (monaxon) spinispirae, I have tried nevertheless to produce proofs for my statement by carefully studying the spicules treated in various ways. More especially I was led to do this in order to settle the question between Lendenfeld and Topsent about the sponge, which Oscar Schmidt first described under the name of *Tethya bistellata.* Is it, as Lendenfeld suggests, a species of *Spirastrella*, or, as Topsent believes, one of *Hymedesmia?* Of course it is *no Tethya;* so far everybody agrees.

Schmidt (1862 p. 45) described a sponge, which he called *Tethya bistellata*, a name which he altered himself into *Suberites bistellatus* (1864 p. 36). Now Lendenfeld believed to have traced the sponge in his collection from Lesina and called it *Spirastrella bistellata* (1897 p. 55). From this Topsent dissented in 1898, alleging that

Tethya bistellata O. S. must be transferred to *Hymedesmia*, and consequently he called it *Hymedesmia bistellata* (1900 p. 125)[1]).

Now I possess in my collection from Naples a sponge, which is beyond reasonable doubt SCHMIDT's *Tethya bistellata*. I can affirm this especially because the spicules *absolutely agree* with those of a preparation I made at the time in Graz and which is labelled "*Suberites bistellatus* O. S. Origin. Schmidt." We may suppose, therefore, that LENDENFELD, TOPSENT and myself really examined the same sort of spicules, albeit that I must acknowledge that there is no *absolute* proof.

TOPSENT says, that the microsclera under consideration are euasters; he writes (1900 p. 123) that they are "sphèrasters de forme particulière . . . Chacune d'elles résulte de la congrescence latérale de deux sphèrasters à actines nombreuses, coniques, pointues et lisses." And later (p. 127): "les sphèrasters sont doubles. O. SCHMIDT a insisté sur ce caractère important, auquel l'espèce doit son nom." The question arises whether SCHMIDT's statement is of great value. In 1862 he said (p. 45) that some are "ganz eigenthümliche Zwillingsgestalten"; and further: "es sind also Doppelfiguren, welche einige Aehnlichkeit mit den Euastern haben." It must, however, not be forgotten that SCHMIDT at that time was unconcious of the sort of spicula which he called later (1868 p. 17) "Spiralsterne" or "Walzensterne" of which he mentions as characteristic "dass ihre Strahlen nicht Radien eines Centrum sind, sondern in Spiralstellung sich folgen."

According to LENDENFELD (1897) are the spicules under consideration "spirasters" and he gives some illustrations (l. c. Pl. VI fig. 59) which clearly show his conception of the thing. Both from his illustrations and from his description it follows that the axis is sometimes longer, sometimes shorter. LENDENFELD does not believe that "euasters" occur and suggests that SCHMIDT was perhaps misled by an optical illusion. If spicules are examined "deren Axen im Praeparat aufrecht stehen und daher verkürzt gesehen werden" they *simulate* euasters.

In spite of the fact that TOPSENT himself remarks, that in minute microsclera it is much more obvious that the centre is a line and not a point, this author does not consider them as spirasters but as double euasters. "Plus elles grandissent, plus la tige d'union se raccourcit. Sur les plus grosses, les deux centrums sont directement accolés . . ." Of course **Topsent** has not overlooked that spicula have a different appearance whether seen "de profil" or "de face"; but evidently he did not pay attention to intermediate positions such as can be seen if one allows them to turn over. I drew attention (1902 p. 170) to the fact that in almost all cases the twisted character becomes plain enough by applying the above device.

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[1]) Actually the course of events was this: TOPSENT (1900 p. 113) writes with regard to *Tethya bistellata O. S.*: "je l'ai mise à sa place naturelle en 1892." However, in that article nothing is mentioned but the name *Hymedesmia bistellata without reference to Tethya bistellata.*

However, there are some more methods to make out the shape and the structure of spicules (Cf. **Vosmaer** & **Wijsman**, 1905 p. 745).

One of these methods is heating. In using this method it is, however, not indifferent in what way it is applied. If isolated spicules (e. g. styli of *Tethya*) simply dried in the air, are heated on a platina spatula immediately above the flame, a brownish colour soon becomes visible. If they are further heated the brownish tinge turns into white. It then frequently occurs that a crackling noise is heard and that spicules or portions of spicules jump off from the spatula. Such spicules, seen under the microscope, generally appear to be cracked or broken; they are brown or black, some were quite misshapen as if the spicopal had been partly melted.

How can these phenoma be explained? **Bowerbank** ascribed the brown or black colour to carbonised organic matter, but **Kölliker** proved that the colour can certainly not wholly be explained in this way. Indeed, in some parts the colour is brown only in transmitted light, whereas it is white in reflected light; consequently **Kölliker** declared those parts to contain microscopical air-bubbles. Quite correctly **Bütschli** (1901 p. 240) remarks that **Kölliker** where he speaks of "Luft", in fact means "Gas". **Wijsman** and myself have demonstrated (1905 p. 28), that spicopal is a form of hydrated siliceous acid, which can give off water in an atmosphere dried by P_2O_5. It is, therefore, very likely that when the spicules are treated as described above, a portion of the water becomes water-vapour. The tension of the heated globules of steam of course can be great enough to make the spicule explode. This explains at the same time the crackling noise and the jumping off from the spatula. Still, it *need not* come to this; hence we see some spicules only slightly cracked, not broken or deformed.

If, however, spicules are not simply dried in the air, but, by slowly warming on asbestus for several days or by P_2O_5, water is taken from them, and they are afterwards very carefully heated, then it is possible to prevent any cracking. Spicules treated in this way show quite other details. First of all the carbonised central thread is clearly visible. In some spicules the rest of the spiculum remained quite transparent; in others a brownish colour is to be seen on special places. Seen with reflected light these places are white; on the whole those places have a granular or frothy appearance. [1]) As a rule the lamellar structure is very conspicuous. In certain cases the carbonised spiculum sheath is likewise visible. It also happens that the carbonised and shrunken central thread is seen as a flexuous, continuous or broken, black string lying within the central canal (fig. 20—21). Of course the best microscopical figures are obtained if the spicules are examined in a medium the index of refraction of which is equal to or comes very near that of the spicopal.

Controlling experiments sufficiently prove that no artefacts or anything of that sort come into play through which no conclusion can be drawn about the structure of the spicule. The spicopal being in slowly by dissolved the method published by Wijsman and myself, the microscope reveals facts which are in perfect accordance with those obtained in the way described above. One may also combine the two methods — heating and dissolving; again the results are the same if one follows the process under the microscope. Suppose one observes in heated spicules a black central thread with a brownish surrounding; suppose the object is mounted in glycerine of about the same index of refraction as the spicopal, the external limit is clearly visible as a delicate dark line (fig. 22). Some time after the action of the hydrofluoric acid the spicule appears as drawn in fig. 23. The silica begins to be dissolved as soon as the hydrofluoric acid has penetrated the spiculum sheath; the external delicate line remains visible but at some distance the limit of the spicopal, now thinner, becomes visible. The distance between the sheath and the limit of spicopal becomes gradually larger, the brownish surrounding of the central thread disappears and finally nothing is left but the carbonised central thread and the likewise carbonised sheath (fig. 24). This proves, that the brownish colour arround the axial thread does not originate from carbonised organic matter.

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[1]) Bütschli admits as is well known, that in spicules which are not heated likewise little holes occur and that these holes simply become larger by the process of heating and consequently better visible. He says (l.c p. 248): "Das Auftreten der feinwabigen Struktur beruht darauf, dass eine solche auch schon in der nicht geglühten Nadel besteht, jedoch zu fein, um mikroskopisch sichtbar zu sein. Beim Glühen tritt eine Verdampfung des in den Wabenhohlräumchen eingeschlossenen Wassers ein und damit eine Erweiterung derselben bis zur Sichtbarkeit. Für diese Ansicht spricht vor Allem die Beobachtung, dass wenigstens in einem Fall auch eine nicht geglühte Nadel .... den wabigen Bau der Schichten deutlich zeigte." Apart from the question whether in unheated spicules a frothy structure really occurs or not, it is certain that the dark colour of heated spicules is due to little holes, void of air or filled with some gas, say water-vapour.

The experiment can be modified in the following way. Isolated spicula are brought into acid fuchsine; if the hydrofluoric acid is now allowed to act on the spicules the spicopal will be dissolved, whereas the sheath and the central thread will be stained red. In both cases the silica is dissolved; in the former case the thread and the sheath are visible because they are black (carbonised), in the latter case because they are red. In the original experiment the spicopal is only optically dissolved.

What has been said for the styli of *Tethya* holds true m.m. for other spicules of Demoterellida. The structure of several spicules — monaxons, tetraxons or polyaxons — is fundamentally the same; in details there are important differences. However, I do not wish to speak about them in this paper. I have only mentioned as much as seemed to be necessary to show that by the described methods we are able to demonstrate most plainly the central thread. This can be done also in those cases in which the thread is not visible under ordinary circumstances, e.g. if the spicules are very minute or irregularities of the surface prevent it. Thus, for instance, in *Tethya* no central threads are visible in the oxyasters or at any rate they are not present beyond doubt[1]). If these spicules are heated with great precaution they look under the microscope like fig. 19. It depends, as in other spicules, on the grade on heating whether the thread will be blackened only or with it its surroundings. Independently of this it is evident that the axes originate from one point.

Applying the heating method to the spicules in question of *Spirastrella bistellata* (O. S.) Ldfd. the microscope reveals pictures as drawn in fig. 1—3. It is most evident that we have here an axis exactly like that which unquestionable spinispirae possess. Such images are entirely unexplainable if the spicules are considered as congrescences of two euasters. They fully exhibit their true nature of spicules belonging to my group of α-spiraxons (1902 p. 112). Although I suppose this to be convincing, I applied moreover the dissolving method. It seems rather a paradox that the shape and the structure of a siliceous spicule can be cleared up by dissolving the silica. Still it is a fact, as I have frequently learned. WIJSMAN and myself (1905 p. 18) confirmed BÜTSCHLI's observations of 1901, that the dissolution of spicopal may proceed in more than one way. Only we have given another explanation of the fact. According to our conception the spicopal which limits the central canal is more easily dissolved than that of subsequent layers. It seems that this is likewise the case for the radii of oxyasters of *Tethya*. It is probable that this depends on a difference in the quantity of water the "gel" contains. Now we observed that in pointed undamaged spicules, where consequently the central canal is shut, the funnelshaped dissolution is not seen, at any rate not at the very beginning of the process. The apex simply becomes thinner and thinner till the dissolving agent reaches the neighbourhood of the central canal, in which case the "funnel" often appears. Consequently we have herein another method to prove the existence of a central canal.

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[1]) On the whole spongiologists speak about the central thread as a constant feature of spicules. As a matter of fact stands that the presence of a thread is proved only in some cases and that in numerous microscleres nobody saw it. As far as I know only KÖLLIKER found it in oxyasters of *Tethya* (1864, Pl. IX, fig. 2).

On the other hand we may conclude from this, that, if a funnel never appears there is no central canal resp. no special layer of spicopal in the centre. Thus, for example, in spicules with spines, the latter disappear gradually and the spicule becomes gradually thinner. I have observed this phenomenon very distinctly in acanthostyli of an *Ectyon* from Naples.

If the latter method is now applied on *Spirastrella bistellata* (O.S.) Ldfd. we see, that the pointed processes of the spinispirae become thinner and shorter, and finally disappear whereas the rest of the spiculum later becomes thinner (fig. 4—18). The microscopical images one sees during this process leave no doubt with regard to their structure. The more the spines dissolve, the more it becomes evident that we have to do with spinispirae.

Moreover, it follows from the above experiments that the spines of these spinispirae are of quite another nature than the actines of the *Tethya*-asters. In the former case (*Spirastrella*) we have to do with local extuberances of spicopal destitute of any central thread or canal. In the latter case (*Tethya*) we have organic axes. Indeed, the former spicules are monaxons, the latter are polyaxons.

Consequently the microsclera of *Spirastrella bistellata* (O.S.) Ldfd. are indeed spinispirae. Since LENDENFELD, TOPSENT and myself believe to have found sponges, which are identical with *Tethya bistellata* of OSCAR SCHMIDT, the species belongs as little to *Hymedesmia* as to *Tethya*. For the moment there is not sufficient evidence not to bring it to *Spirastrella*. The name for *Tethya bistellata* O. S. has to be, therefore, *Spirastrella bistellata* (O. S.) Ldfd. I believe with TOPSENT that it is identical with *Spirastrella cunctatrix* O. S.

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EXPLANATION OF THE PLATE.

(Fig. 1—21 are drawn 500 times magnified; fig. 22—24 still more magnified).

Fig. 1—3 *Spirastrella bistellata*; spinispirae carefully heated. In 3*a* only the central thread (carbonised) is drawn, lying in the central canal.

Fig. 4—18 Id. Influence of hydrofluoric acid. In figs. 4, 5 and 6 the acid has acted for a short time; only the spines begin to be dissolved. In fig. 7—12 the process is advanced; the "axis" becomes more and more obvious. In fig. 13—16 this is still more the case.

Fig. 19 *Tethya lyncurium*; oxyaster after carefully heating; distinct, (carbonised) central thread.

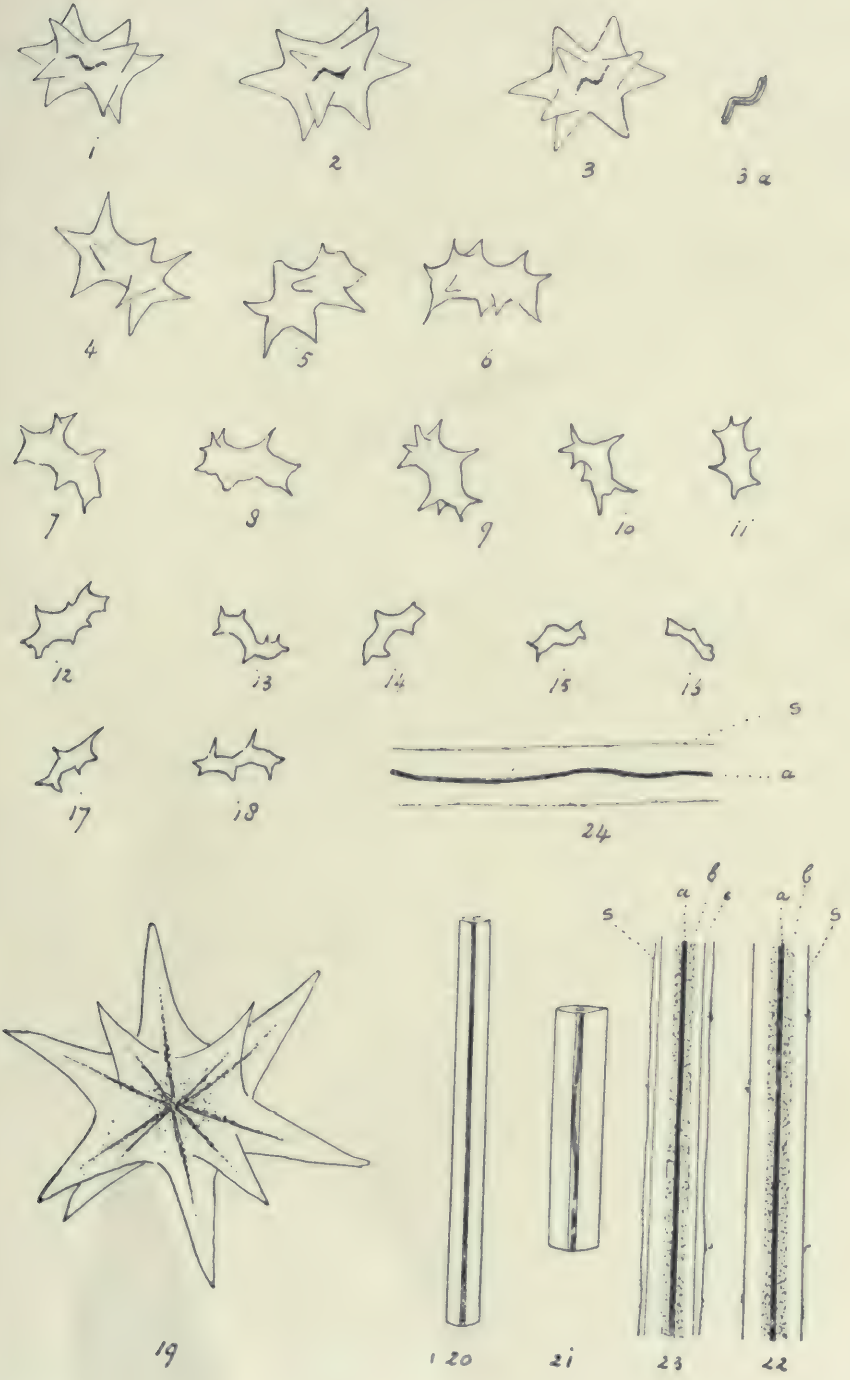
Fig. 20 Id. Middle piece of a stylus, carefully heated. Black (carbonised) central thread, entirely filling up the central canal.

Fig 21. Id. Id. Shrunken, bent and broken central thread in the somewhat brownish central canal.

Fig. 22—24 Id. Id. Slightly more heated and brought into the hydrofluoric camera of Vosmaer & Wijsman; *a*. central thread, *b*. brownish layer around the central canal, *s*. brownish spiculum sheath. In fig. 22 it is seen at the beginning of the experiment; the sheath lies immediately on the external spicopal; the little granula are adhering particles, not belonging to the spiculum. In fig. 23 the hydrofluoric acid has penetrated the sheath and dissolved the peripheral layers of spicopal, the limits of which are marked *c*; the sheath remained in its place. In fig. 24 all spicopal is dissolved; only the carbonised sheath *s* lies as a very delicate cylinder around the central thread.

Leiden, 2 Jan. 1909.

G. C. J. VOSMAER. "On the spinispirae of Spirastrella bistellata (O.S.) Ldfd."



Botany. — Prof. J. W. Moll presents the dissertation of Mr. K. Zijlstra, Assistant at the Botanical Laboratory, Groningen, entitled: "*Kohlensäuretransport in Blättern*", Groningen, 1909, and with reference to this he communicates the following. [1])

In 1877 the speaker published the results[2]) of investigations, which proved, that the carbon dioxide, which is found in considerable quantity in soils containing much humus, and which is at the disposal of the roots, cannot lead to starch-formation in the leaves, when the latter are in a space, free from carbon dioxide; nor can this carbon dioxide appreciably accelerate starch-formation in the open air.

From the experiments, which led the speaker to this result, he further concluded, that a leaf or a portion of a leaf cannot form starch in a space devoid of carbon dioxide, even when parts, organically connected with, and bordering immediately on the portion in question, are placed in an atmosphere which is many times as rich in carbon dioxide as ordinary air. The experiment, which appeared to prove that starch cannot be formed even from carbon dioxide, which is offered to immediately adjoining parts, was the following.

A starch-free leaf was placed between the greased edges of two similar crystallizing dishes in such a way, that the apex was within the space enclosed by the crystallizing dishes, and the base was outside. The lower crystallizing dish contained potassium hydroxide solution; over the apparatus there was placed a bell-jar, containing air to which about 5 percent of carbon dioxide had been added.

After the leaf had been exposed to the light for some hours, the base was found to contain much starch, but in the upper portion, even right up to the edge of the crystallizing dish, which was 3 mm. thick, no starch whatever had been formed.

From this the speaker concluded that when carbon dioxide is abundantly present in any given part of a leaf, this can nevertheless not lead to starch-formation in an immediately adjoining portion, when the latter is in a space free from carbon dioxide.

This result was remarkable, for the starch-formation in the basal portion proved, that the carbon dioxide, offered to the leaf had indeed been taken up, and the presence of many intercellular spaces in the mesophyll led to the supposition, that the transport of the carbon dioxide so taken up, need not be impossible.

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[1]) This dissertation will appear in one of the future numbers of the Recueil des Travaux Botaniques Néerlandais.

[2]) J. W. Moll. Ueber den Ursprung des Kohlenstoffs der Pflanzen. Landwirthsch. Jahrb. VI. 1877. p. 327—363.

A want of further experimental data made this question remain unsolved up to the present. The necessary data have now, however, been collected in the investigation of Mr. Zijlstra, who has shown that the facts, previously observed by the speaker, had indeed been correctly described, but that other results may also be obtained, provided one works with different plants from those which the speaker happened to have used, or arranges the experiments in a different way. Mr. Zijlstra was able to show that in the experiment described, starch-formation may sometimes indeed occur in the space free from carbon dioxide. The above conclusion as to the impossibility of starch-formation at the expense of carbon dioxide derived from the immediate vicinity, has therefore been found to be incorrect. The other results formerly obtained by the speaker, and especially the chief deduction, regarding the impossibility of starch-formation in the leaves at the expense of carbon dioxide, taken up by the roots from a soil rich in humus, were, however, completely confirmed and further elucidated by Mr. Zijlstra's investigation. An explanation of the experiment described above, was also suggested and generally speaking Mr. Zijlstra succeeded in solving pretty completely the question of the possibility and occurrence of carbon dioxide transport in leaves. How this was done the speaker wishes to communicate below.

Not unnaturally it seemed desirable to begin the investigation with a repetition of the above described experiments.

This was first done with the leaves of *Polygonum Bistorta* and of *Cucurbita Pepo* (experiment LIII and LIV)[1]), which were also employed by the speaker in his above-mentioned investigation. In these and in all later experiments Mr. Zijlstra demonstrated the formation of starch by the so-called Sachs-Schimper method, according to which the entire leaves, after decolorisation, are examined for starch content with the help of an iodine-chloralhydrate solution. This method was unknown in 1877, so that the speaker used microscopic sections, which is very cumbrous and gives less complete, albeit equally certain results.

The speaker limited himself to applying the starch reaction to sections of the apex of the leaf, which was in the space free from carbon dioxide, and to the base, which was in the air rich in carbon dioxide. He did not, however, examine the strip, 3 millimeters broad, which was in the grease between the edges of the crystallizing dishes. Now when Mr. Zijlstra examined the entire leaves, it became apparent that starch-formation extended continuously from the leaf base upwards over part of this strip, in an area bounded by a sharply defined line, somewhat like a zig-zag, but that it nowhere extended so far, that starch had also been formed in the space, free from carbon dioxide. The speaker's observations were therefore confirmed, but were found to have been incomplete.

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[1]) The numbers of the experiments are here and in what follows the same as those in Mr. Zijlstra's paper.

When, however, Mr. Zijlstra repeated the experiment with a *Dahlia* leaf (exp. LV) the result was different. In this case also the starch-formation was found to extend into the greased strip, but in addition it extended here and there for some millimeters into the space freed from carbon dioxide. The border line of the starch reaction was here also somewhat zig-zag, but not everywhere equally sharp.

Finally, when the experiment was performed with a leaf of *Pontederia cordata* (exp. LVI) starch-formation extended uniformly for 0.5 centimeters into the carbon dioxide free space. The limit of the starch reaction was in this case not zig-zag, but bent regularly and was not sharp, since the dark colour of the reaction disappeared towards the leaf apex by a gradual transition. Stahl's cobalt test showed, that the stomata of the apex were closed at the end of the experiment.

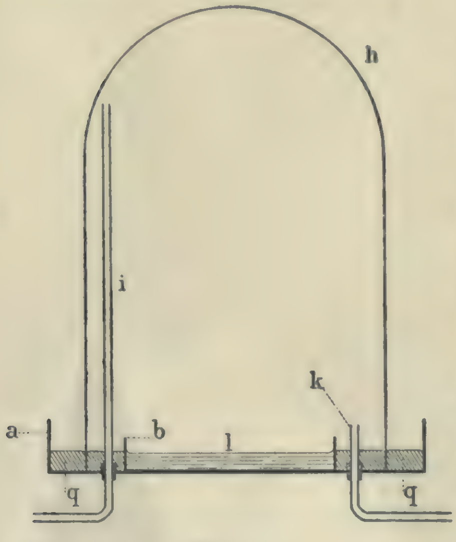


Figure 1.

The possibility now existed that in these experiments the greased join had not been absolutely tight, although it was not very probable that this fault should have revealed itself in the experiments with *Dahlia* and *Pontederia* and not in others. In order to exclude this possibility two pieces of apparatus were constructed, which, with the aid of mercury, permitted of a completely airtight separation being effected between the space free from, and that rich in carbon dioxide. Both pieces of apparatus were used in the investigation, but here the speaker will only describe the better of the two. (See fig. 1).

In a Petri dish *a*, of 15.5 cm. diameter a smaller one *b* of

9 cm. diameter was fastened down with resin and wax. Mercury was poured into the annular space *q* and concentrated caustic potash into the small Petri dish *l*. A glass bell-jar *h* of 3.2 litres' capacity was placed in the mercury, so that the air inside the jar was kept free from carbon dioxide. It was now possible to introduce the apex of a leaf, which had been freed from starch, into the carbon dioxide-free space through the mercury. The leaf base and the petiole thus remained outside the bell-jar *h*, and the petiole was always immersed in a dish of water in order to keep the leaf fresh throughout the experiment. A piece of metallic gauze was always placed over the small Petri dish *b* in order to prevent the leaf from coming into contact with the caustic potash. The base of the leaf could now be left at will in the open air with its unlimited supply of carbon dioxide at great dilution, or the base could be surrounded with an atmosphere richer in carbon dioxide. For the latter purpose the whole apparatus was placed on a tripod in a large porcelain dish, partly filled with water. A large glass bell-jar of 38 litres' capacity was placed over the apparatus containing the leaf, so that the space in the large bell-jar was cut off by the water in the porcelain dish. Into this space any desired quantity of carbon dioxide could be introduced. Finally attention may be drawn to the tubes *i* and *k*, which connected the interior of the small jar with the free atmosphere. This prevented differences of pressure between the interior and the exterior from raising the jar and establishing a communication between the outside and the inside. Moreover a stream of air, free from carbon dioxide, could be passed by these tubes through the inner jar. For this purpose the tube *k* was connected to an aspirator, and the tube *i* to absorption tubes for the carbon dioxide of the atmosphere.

With this apparatus a number of experiments were carried out, in some of which the base of the leaf was in the ordinary atmosphere, and in others in an atmosphere with much carbon dioxide. The portion of the leaves which was underneath the mercury had in all the experiments a length of 3 centimeters. These experiments led to the result, that not only in *Dahlia* and *Pontederia* leaves but also in all the other leaves investigated, a narrow strip of starch was formed in the space free from carbon dioxide at the border of the mercury. This strip was generally coloured jet black by iodine.

The following table summarizes a number of experiments performed in this manner.

In all these experiments the small starch strip was of course bordered on the side of the mercury by a straight line, but towards the apex

TABLE I.

Plant.	Number of exp.	The leaf base in:	Duration of exp.	Width of the starch strip.
Dahlia Yuarezii	I	5 % CO^2	5 hours	3 mm.
„ „	II	open air	5 „	2—3 „
„ *(Cactus) Thuringia*	XVI	2 % CO^2	5 „	3—4 „
Aster macrophyllus	V	open air	4 „	0.5 „
Sisymbrium Alliaria	VI	„ „	5 „	1 „
„ „	X	„ „	4 „	1.5 „
Polygonum Bistorta	VII	„ „	4 „	3 „
Aesculus Hippocastanum	VIII	„ „	4 „	0.5 „
„ *Pavia*	IX	„ „	3 „	0.5 „
Acer campestre	X	„ „	4 „	0.5 „
Sambucus nigra	XII	$2\frac{1}{2}$ % CO^2	5 „	2 „
„ „	XIII	„ „	5 „	3 „
Juglans regia	XIV	2 % „	6 „	1 „
Acorus Calamus	XV	„ »	7 „	2 „
Heliopsis laevis	XVII	$2\frac{1}{2}$ % „	6 „	1.5 „

of the leaf the border was a zig-zag line, which often coincided with the presence of veins in the leaf. In those places the border-line was sharply defined. In *Acorus* alone this line was also straight, without clearly depending on the veins; in this case moreover, the border line was not sharp, but towards the apex the reaction became weaker by imperceptible degrees and soon disappeared completely.

Since in these experiments the apex of the leaf was in a space free from carbon dioxide we must assume, that the starch strip had been formed at the expense of the carbon dioxide, which had been transported from the portions of the leaf nearer the base.

The most plausible assumption now seemed to be the following: that the carbon dioxide which had been absorbed by the leaf base, had been conducted through the parts of the leaf under the mercury, and having arrived in the part of the leaf exposed to the light, had there given rise to the formation of starch. In order to test the validity of this assumption, comparative experiments were undertaken, in which the one leaf was placed with its base in air containing

2—3% of carbon dioxide, and the other in ordinary air, containing therefore very little carbon dioxide.

If the hypothesis just brought forward were correct, one might expect that owing to a more copious supply of carbon dioxide, a wider strip of starch would be formed in the former case than in the latter. It did not seem probable that the increased supply of carbon dioxide would manifest itself by a stronger iodine reaction, for, as we have seen, in most of the experiments described above, the reaction, if it appeared at all, was as strong as possible.

These comparative experiments were carried out with two sets of apparatus of the kind described, both of which were provided with a large bell-jar, including therefore the one in which the leaf-base was in ordinary air. This was done in order to maintain as far as possible the same temperature in the two smaller jars, for it was found that in these experiments the temperature had a great influence on starch-formation.

The result of these experiments varied considerably in different plants. In some cases it could be definitely shown, that carbon dioxide, supplied to the base, had influenced the manufacture of starch in the upper part of the leaf, but this could not be demonstrated for other plants.

The speaker first considers the experiments with a positive result, summarized in the following table:

TABLE II.

Name.	Number of experiment.	Duration of experiment.	Width of the starch strip in the CO_2 free space.	
			Base in 2% CO_2.	Base in ordinary air.
Pontederia montevidensis	XLVIII	7 hours	6 mm.	2 mm.
Eichhornia speciosa	XLIX	7 „	1 cm.	2 „
„ „	L	$5^1/_2$ „	1.5 „	1 „
Eucomis punctata	LI	9 „	1 „	3 „

The first two experiments were carried out with leaves which were as nearly as possible equal, and the last two each with the halves of one and the same leaf.

All these experiments very clearly demonstrate the influence of the increased supply of carbon dioxide by the formation of wider strips of starch.

In the above experiments the leaf base in the space with much carbon dioxide was exposed to the light and accordingly this part of the leaf was full of starch at the end of the experiment. We might now expect that on darkening the leaf-base, more carbon dioxide would remain available for transport to the apex, and that a wider strip of starch would be formed than in the former case. If this expectation were realized, it would be an additional proof, that carbon dioxide is transported from the base to the apex. An experiment, carried out with the two longitudinal halves of the same leaf of *Eichhornia* (exp. LII) indeed gave proof of this. Here both bases were kept in air with 2 °/₀ carbon dioxide, but one was darkened, the other not. In the latter case less carbon dioxide remained available for transport on account of the consumption of carbon dioxide for starch-formation in the base, and in the course of 4 hours a strip of starch , 2 - 5 mm. wide, was formed in the upper part of the control half, as compared with one 5—8 mm. wide in the other half of the leaf, of which the base had been darkened.

In these experiments the strip of starch never had anything like a sharp edge on its upper side, nor was there any connexion between the limit of the reaction and the veins. The reaction simply became weaker and weaker at the edge of the strip and soon stopped completely.

A series of experiments with other leaves yielded, however, a totally different result. Here the strip of starch in the two leaves experimented on was always equally wide, no matter whether the leaf base had been placed in ordinary air or in air with a high carbon dioxide content.

In some of these experiments leaves of the same plant individual were taken, in each case as nearly as possible equal. The subjoined table summarizes them.

TABLE III.

Plant.	Number of exp.	Duration of exp.	Width of the starch strip in both leaves.
Sambucus nigra	XIX	5 hours	3 mm.
Juglans regia	XX	6 „	1 „
Acorus Calamus	XXI	7 „	2 „
Zea Mays	XXII	6 „	1.5 „
Hordeum vulgare	XXIII	7 „	1 „

The negative result thus obtained, could now, after the experience with the influence of darkening on the leaf base of *Eichhornia* in experiment LII, be attributed to the fact, that the carbon dioxide absorbed by the base, had been wholly used up for starch-formation on the spot. Experiments were therefore also made, in which the leaf bases were darkened with black paper right up to the edge of the mercury, and therefore remained free from starch. But these experiments also gave exactly the same result; the strips of starch were equally wide in the leaves with bases in air containing much carbon dioxide, as in those with their bases in ordinary air.

A survey of these experiments is given in the subjoined table:

TABLE IV.

Plant.	Number of exp.	Duration of exp.	Width of starch strip in both leaves.
Triticum vulgare	XXIV	6 hours	1.5 mm.
Zea Mays	XXV	6 „	2.5 „
Dahlia Yuarezii	XXVI	5 „	4 „
Aesculus Pavia	XXVII	4 „	< 0.5 „
Tradescantia virginiana	XXVIII	4 „	1 „

In order to eliminate more thoroughly possible inequalities between the leaves compared than could be done by careful choice, a few experiments were also performed, in which the longitudinal halves of the same leaf were used for comparison, and were darkened at the base. These experiments yielded the same result, as given below:

TABLE V.

Plant.	Number of exp.	Duration of exp.	Width of starch strip in both halves of leaves.
Dahlia (Cactus) Thuringia	XXIX	5 hours	not noted
Heliopsis laevis	XXX	6 „	1.5 mm.

Finally two experiments may be mentioned, which were performed under conditions, similar to those of the last named, but in which the caustic potash was omitted in the smaller bell-jar. In all the previous experiments the carbon dioxide of the leaf apex would, if it were at all possible diffuse into the surrounding space, which remained permanently free from carbon dioxide. This, however, did evidently not take place so fast, but that in all experiments starch was formed near the mercury.

Nevertheless the possibility was not excluded, that a wider strip of starch might appear, if the carbon dioxide absorbing potash were absent.

Such experiments were accordingly undertaken, and in order to make it possible that there should even be some accumulation of transported carbon dioxide, the inner bell-jar of the apparatus, which hitherto had been of a capacity of 3.2 litres, was replaced by one of only 0.8 litres' capacity.

In both experiments two halves of the same leaf were taken in each case. The two bases were placed in 3 °/₀ carbon dioxide, one being exposed to the light and the other darkened. The two halves gave exactly the same result and the starch strips were not wider than in all the previous experiments, as is shown by the following summary:

TABLE VI.

Plant.	Number of exp.	Duration of exp.	Width of starch strip in both halves of leaves.
Dahlia (Cactus) Thuringia	XXXI	4 hours	3—4 mm.
Heliopsis laevis	XXXII	4 „	0.5—1 „

It is obvious from all these experiments that with a number of leaves from widely different *Monocotyledons* and *Dicotyledons* a totally different result is obtained from that of the experiments described first. Carbon dioxide, even when abundantly supplied to the leaf base of these plants, cannot bring about the formation, at about 3 cm. distance in the apex of the leaf, of a wider strip of starch, than would have been formed without the addition of this carbon dioxide. Attention may further be drawn to a difference, which again clearly showed itself in these experiments, between the reticulate *Dicotyledons* and the parallel-veined *Monocotyledons* as regards the edge of the starch strips on the side nearest the apex. In all leaves with reticulate venation these edges were zig-zag and in most places sharply defined, owing to the presence of small veins. In the leaves of *Grasses*, of *Acorus* and of *Tradescantia* on the other hand there was a gradual transition to the starch-free apical portion, without any relation to veins, and there was no zig-zag border.

It would certainly be going too far to deduce directly from these experiments, that the carbon dioxide, which is supplied to the base of these leaves, cannot at all contribute to starch-formation in the apex. Nevertheless the results obtained gave a clear indication as to further experiment, intended to show, beyond dispute, if possible, what was the state of affairs in these leaves.

The way in which such experiments should be performed was now clear.

The base of the leaf must be deprived of any supply of carbon dioxide, and the question was whether, as might almost have been expected from the above, a strip of starch would be formed above the mercury. If this were to take place, and in the same way as before, the proof would have been given, that the part of the leaf, placed under the mercury, itself produced the carbon dioxide, required for starch-formation in the adjoining part, which was exposed to light.

The experiments which supplied an answer to this question were made by Mr. Zijlstra in various ways.

In the first place an experiment was made with the apparatus described above, but without the large bell-jar. A small leaf of *Dahlia Yuarezii* (exp. XXXIII) was placed in the apparatus in the ordinary way, but the base and the petiole were immersed in water which had been poured on the mercury outside the small jar. In the space free from carbon dioxide the apex now produced a strip of starch, similar in all respects to that in the experiments previously described, and in addition, a starch strip was formed under water in that part of the base which adjoined the mercury.

Similar experiments were also made with a simpler apparatus, which moreover permitted of the water, in which the leaf base was placed, being kept quite free from carbon dioxide.

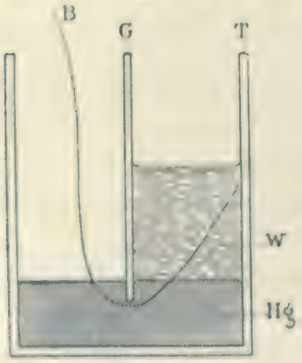


Figure 2.

Fig 2 gives a representation of this little apparatus. It consisted of a rectangular glass box, measuring 9 by 4.5 cm., and 5 cm. high, which is represented in the figure in section, the wall being indicated by *T*. With resin and wax a vertical plate of glass was fixed longitudinally but it did not reach to the bottom. The box was filled with mercury to slightly above the lower edge of the glass plate *G*. The leaf *B* was introduced underneath the vertical plate, so that its base was on the right side of the figure. There a layer of boiled water *W* was poured on the mercury, so that the base was completely submerged. The apparatus was now placed under a bell-jar with air, free from carbon dioxide, and the whole was exposed to the light.

After some hours starch had been formed in this apparatus in *Dahlia Yuarezii* (exp. XXXIV) and in *Populus pyramidalis* (exp. XXXV); there was a strip of starch in the apical portion along the mercury, quite like that of the previous experiments; there was a similar strip in the basal portion under water, also along the edge of the mercury; and finally a narrow strip of starch had appeared in the mercury itself, at the place where the leaf had been in contact with the lower edge of the vertical glass plate and had therefore received light.

The carbon dioxide, which in this case had been used up in starch-formation, could only have been derived from the portions of the leaf under the mercury and could scarcely be anything but carbon dioxide of respiration from these parts.

When this had once become evident, a still simpler arrangement naturally suggested itself. For this purpose pieces of leaves, free from starch, were placed on a layer of mercury, were partially covered with black paper, and finally pressed under the mercury by means of a glass crystallising dish with flat bottom. The light could now reach those parts of the leaves which were not covered by black paper, through the bottom of the glass dish.

Such experiments were made with *Dahlia Yuarezii* (exp. XXXVI, XXXVII and XLI), *Sambucus nigra* (exp. XXXVIII), *Syringa vulgaris* (exp. XXXIX) and *Tilia platyphyllos* (exp. XL). In all these experiments, which lasted about 5 hours, strips of starch were formed in the ordinary way at the border of the black paper in the lighted portions of the leaves; the border of the starch on the side opposite the paper was again sharply defined in many places by veins.

We may hence assume, that in all the experiments of the second group, in which the result was negative, starch had been formed exclusively at the expense of the carbon dioxide, resulting from the respiration of the parts of the leaf under the mercury, which carbon dioxide had been transported a certain distance to those parts, which were exposed to light.

In this case the supply of carbon dioxide from outside was prevented by the mercury, which also kept off the light. The respiratory carbon dioxide could therefore not be immediately reduced on the spot, but could spread and thus reach the lighted portions of the leaf in fairly large quantity. It should further be noted, that the epidermis of the darkened leaf-fragment was closed hermetically by the mercury, so that the carbon dioxide formed could not escape from the leaf, but had to move sideways.

The question now arose whether this closing of the epidermis was a necessary condition for the success of the experiments. From the nature of things this might be considered probable, for otherwise the respiratory carbon dioxide would follow the line of least resistance through the stomata and epidermis. Experiments made with this object in view have completely confirmed this opinion. A leaf of *Dahlia Yuarezii* was introduced into the apparatus first described, with its apex in the small bell-jar without caustic potash. One longitudinal half of the apex was uncovered, but to the other half a strip of black paper was fastened, by which a transverse strip of this half was darkened; this strip measured 17 mm. from the mercury in the direction of the tip (exp. XLII). In the same leaf it was therefore possible to compare: a lighted portion adjoining a darkened one, the epidermis of which was shut off by the mercury; and a lighted portion adjoining one darkened by paper, the epidermis of which was therefore not shut off. A starch zone was indeed formed along the edge of the mercury, but not along that of the black paper. When the experiment was repeated (exp. XLIII), with the portion of the leaf under the paper smeared with a mixture of cocoa-butter and wax (according to STAHL), the result was quite different. This mixture is known to close the epidermis almost completely to carbon dioxide, and the well-known starch zone now also appeared at the edge of the paper.

The use of cocoa-wax finally led to some experiments which may be called extremely simple, and which once more confirmed the result obtained.

Leaves of *Aesculus Pavia* (exp. XLIV) and of *Juglans regia* (exp. XLV), free from starch, were completely covered with cocoa-wax, in which condition, according to STAHL's experiments, extremely little or no starch is formed during exposure to light in the open air. The leaves were, however, exposed to the light by Mr. ZIJLSTRA after they had been partially covered with black paper or tin-foil, and now, as was to be expected, black borders of starch were formed along the edges of the paper and of the tin-foil.

A rather pretty modification of these experiments was finally obtained by using variegated leaves, of which the colourless portions were quite white, and did not therefore contain any carotin, by means of which carbon dioxide might be decomposed, even in the absence of chlorophyll. It is further necessary that such leaves, in order to be suitable for the experiments in question, should possess in their colourless parts a well-developed parenchyma, capable of producing by respiration a proper amount of carbon dioxide. If such leaves, after having been freed from starch, are smeared with cocoa-wax to prevent the escape of the carbon dioxide formed by respiration and are exposed to the light, borders of starch are developed in the green portions, at the edge of the colourless patches, in the same way as in the earlier experiments, but without any portion of the leaf having been darkened. Such experiments were performed with leaves of *Cornus tartarica* and *Elaeagnus Frederici* (exp. XLVI) and the best result was obtained with *Pelargonium zonale* (*Mad. Salleroi*) (exp. XLVII).

It appears from the above, that in all the leaves investigated a transport of carbon dioxide was possible to a greater or lesser extent, and that this might lead to starch-formation in the portions of the leaf exposed to the light. The experiments were arranged in such a manner, that this starch-formation generally showed itself in more or less broad strips of the leaf. But the carbon dioxide which led to the formation of these starch strips was found to be of dual origin.

In the majority of the leaves investigated, and in all the experiments of the various tables, except those of table 2, we had to assume, that the starch strips were exclusively formed at the expense of the respiratory carbon dioxide, which had been formed in the neighbouring darkened portions, hermetically shut off by mercury or by cocoa-wax.

In the experiments with water plants, mentioned in table 2, the respiratory carbon dioxide must no doubt have also contributed to the formation of starch borders. These experiments did show, however, that another source of carbon dioxide also cooperated, namely the supply of carbon dioxide, which had been added to the air surrounding the leaf-base, which was absorbed by this base, and which was transported through the 3 cm. long portion of the leaf under the mercury into the space free from carbon dioxide, and was assimilated there.

In other words: in most leaves, of *Monocotyledons* as well as of *Dicotyledons*, only a very limited transportation of carbon dioxide is possible. But in these leaves one has an excellent method for the study of this transportation, by utilizing the respiratory carbon dioxide of the adjoining parts.

In a few parallel-veined leaves of water plants on the other hand, a much wider transportation is possible, which can be demonstrated with the relatively rough apparatus employed.

The question now arose, how these two varieties of carbon dioxide transportation must be imagined and on what the difference of the two categories of leaves referred to, depended.

Mr. Zijlstra succeeded in giving a complete account of these phenomena by the study of the anatomical structures of the various leaves used in the experiments.

The speaker begins with those cases, constituting the majority, in which starch-formation only took place at the expense of the respiratory carbon dioxide.

The carbon dioxide of respiration, produced by the living cells, will of course diffuse into the intercellular spaces, and as these are connected up for longer or shorter distances, we may indeed assume that a transportation of carbon dioxide will in the first place take place by diffusion along this route.

Further we must consider, that the veins generally have far fewer intercellular spaces than the parenchyma; indeed, they may have none at all.

In this connexion a fact deserves notice, to which repeated attention has already been drawn in the above, namely, that the starch strips were generally sharply defined by veins on the side opposite to the carbon dioxide supply, so that it gave the impression, as if these formed a barrier across which the starch-formation could not extend. The edge of the starch strip was therefore frequently toothed in an irregular manner. In the *Dahlia* leaf, which is coarsely reticulate, the strips of starch came out largest in all experiments; especially in those places where the veins happened to be a little more remote from the border-line between carbon dioxide production and carbon dioxide consumption, the starch had spread furthest, and then there was often no sharp delimitation. In leaves with very fine meshes between the veins, such as those of *Aesculus* and *Acer*, the starch zones were correspondingly narrow.

In parallel-veined *Monocotyledonous* leaves on the other hand, as for instance in the experiments with *Acorus*, *Zea*, *Hordeum*, *Triticum* and *Tradescantia*, there was no relation between the edge of the starch strip and the small transverse veins. On the contrary, in these leaves the starch strip was generally seen to be straight on the side facing the apex of the leaf and not sharply defined; it faded away gradually, albeit fairly rapidly.

These observations led to an anatomical investigation of the various leaves used in the experiments, especially with a view to answering the question, to what extent their veins, in the absence of intercellular spaces, formed barriers, across which the carbon dioxide could not move at all, or only very slowly. Should this really prove to be the case with the leaves employed, then the simplest interpretation of the observed facts would be, that the carbon dioxide can indeed be readily distributed through the intercellular spaces by diffusion, but that this distribution can be limited by the wholly or partially closed tissue of the veins. In that case one would come to the conclusion, that such leaves are divided up by smaller and larger veins into areas, within which carbon dioxide transportation can readily take place. The passage from any one such area to another is difficult however, or quite impossible. The distance across which carbon dioxide can be transported in such a leaf will therefore depend very largely on the average size of the transport areas in the leaf.

The anatomical investigation showed, in the first place, that in the case of net-veined *Dicotyledonous* leaves, the conception which has been worked out above, completely explains the phenomena observed. Mr. ZIJLSTRA indeed found, that in these leaves veins, which take up the whole thickness of the leaf, are devoid of intercellular spaces. A leaf such as that of *Dahlia*, in which similar transverse veins occur only at comparatively long intervals, will have large transport areas, and will be able to form relatively wide strips of starch. On the other hand in leaves like those of *Acer* and *Aesculus*, in which numerous vein branches occur close together, and take up the whole thickness of the leaf, we can only expect to find narrow starch strips such as indeed occur.

The transport areas, even in the *Dahlia* leaf, which is in this respect in the most favourable condition among reticulate leaves, are nevertheless very small, certainly much smaller than 3 cm. in diameter, as simple inspection of the leaf shows. It is therefore evident, that in the first apparatus, in which the part of the leaf under the mercury measured 3 cm., these leaves were bound to give negative results, as regards the conduction of carbon dioxide supplied to the leaf base.

In all experiments with these leaves, an idea of the carbon dioxide transportation could, however, be obtained from the starch-formation which took place at the expense of respiratory carbon dioxide, derived from other parts of the same transport area. It is also evident that in these leaves the edges of the starch strips must often follow the irregular course of the veins and must suddenly cease at the veins. Only in those cases, in which only a small portion of the leaf area was in the dark and so could produce but little carbon dioxide, it might be expected that the large lighted portion could not fill itself completely with starch, and that the edge of the starch strip would not be sharp. Places in which this could be observed, were indeed pretty frequent in *Dahlia* leaves.

An important question now arose, as to the condition of the various parallel-veined leaves, which, in the experiments described above, also formed rather narrow and not very sharply defined starch strips. As regards the grass leaves of *Hordeum*, *Triticum* and *Zea Mays*, the transverse veins, which connect the longitudinal veins, are here indeed insignificant; the vascular bundles by no means fill up the whole thickness of the leaf and much parenchyma remains above and below. Investigation showed, however, that in transverse section the intercellular spaces of this latter parenchyma are very narrow, although they extend pretty far longitudinally. When passing through this parenchyma above and below the veins, the carbon dioxide is therefore checked very much more than in the general parenchyma between the veins, and its course must be much less rapid, although it is not stopped completely. In accordance with this, only narrow starch strips were formed in these leaves in the limited duration of the experiments, which lasted generally for 6, or at most for 7 hours. In other words, the carbon dioxide transportation was very limited, so that a transference of carbon dioxide across a greater interval than 3 cm., in the apparatus first described, was an impossibility. The transverse anastomoses of the veins did not however, sharply define the starch strips.

The leaves of *Acorus* and *Tradescantia* behaved similarly in the experiments performed. In the green parenchyma of *Acorus* only small intercellular spaces occur and here some veins moreover take up the whole thickness of the leaf, the colourless central parenchyma of the leaf contains it is true many large spaces which extend longitudinally, but at frequent intervals they are shut off by transverse cell-layers, diaphragms without intercellular spaces. Lastly *Tradescantia* has a very spongy assimilating tissue, but in it many vein-anastomoses occur, which only have minute intercellular spaces. In these cases too therefore the agreement between the anatomical structure and the experimental result was sufficient to warrant the acceptance of the above view.

Finally the question arose how the intercellular spaces are distributed in the leaves of *Pontederia*, *Eucomis* and *Eichhornia*, which, as is evident from the experiments of table 2, are much better adapted for carbon dioxide transportation, so that in the apparatus employed this gas could be carried from the leaf base to the apex.

The anatomical investigation of these leaves yielded the following result. The leaf of *Eucomis* is parallel-veined, the whole of the leaf-parenchyma is very spongy, and the longitudinal as well as the transverse veins are very insignificant, so that carbon dioxide can everywhere pass freely. There are still better gas passages in the curved-veined leaves of *Eichhornia* and *Pontederia*. In both these species the parenchyma contains air-channels, running continuously from the base to the apex and taking up from one third to one half of the area of a transverse section. In these channels there are, it is true, diaphragms of one cell thick, but these are themselves also provided with many wide intercellular spaces.

It is therefore merely a matter of course, that in these leaves carbon dioxide can be carried over much larger distances; indeed, it is clear that this carriage could extend from the lowest part of the base to the very tip, given a sufficient duration and suitable arrangement of the experiments.

It is likewise quite natural, that no veins form a sharp boundary to the starch strips on the side towards the leaf apex.

These observations therefore also completely confirmed the view, that the above conception of carbon dioxide transport in leaves is the correct one.

At the same time it will be clear that fundamentally this representation is the same for all the leaves examined. In net-veined leaves the transport areas are small and very sharply defined; in the parallel-veined leaves of *Grasses*, *Acorus* and *Tradescantia* they are small but less sharply defined; in the leaves of *Eichhornia*, *Eucomis* and *Pontederia* the whole leaf is one transport area. If it were possible to make experiments with the two first-named categories of leaves in an apparatus of the first type described, but of much smaller size, positive results as regards carbon dioxide transportation would then be obtained as readily as has now been the case with leaves of the third category only.

Lastly there is the question over what distance the carbon dioxide transport can extend in various leaves.

We have seen that in *Eucomis*, *Pontederia* and *Eichhornia* carbon dioxide can be transported through a piece of leaf 3 cm. long under mercury and then even 1.5 cm. farther through the apical portion, which was placed in air, free from carbon dioxide and of which the stomata were closed. As has already been said, we may assume that this distance is by no means the maximum one, but that it might be increased at will, on condition that the duration of the experiment were also increased as much as possible.

In all the other leaves, however, it was found that the carbon dioxide could not reach the apex through the 3 cm. long portion. With some of these leaves experiments were now made in order to determine the maximum distance, through which carbon dioxide could be transported during the course of the experiment. These experiments were arranged as follows. The leaves, freed from starch, were completely covered with cocoa-wax and then, here and there, with strips of paper of various widths; between these strips portions of the leaf remained exposed to the light.

Borders of starch were then formed along both sides of the black strips of paper, since the respiratory carbon dioxide, formed under the paper, escaped on both sides. The width of these starch borders was slight in the case of the narrowest strips of paper, because beneath these but little carbon dioxide was formed; it increased with the width of the strips and of course reached its maximum as soon as the half-width of the black strip of paper corresponded more or less to the maximum distance through which carbon dioxide could pass during the time of the experiment. The half-width of that strip of paper, at which the starch borders just reached their maximum width, was therefore a measure of the distance through which the carbon dioxide in the leaf could pass under the given conditions.

Such experiments were first made with parallel-veined leaves, in which the carbon dioxide transport was only limited by the small dimensions of the intercellular spaces. The result was, that in *Triticum* (exp. LVII) the carbon dioxide could be transported in 6 hours over at least 2.5 cm., in *Acorus* (exp. LVIII) in 6 hours over rather more than 1 cm., in *Tradescantia* (exp. LIX) in 5 hours over less than 1.5 cm. There is every reason for the assumption, that in these leaves, in experiments of longer duration, somewhat higher values might have been obtained.

In net-veined *Dicotyledonous* leaves the case is somewhat different, for, as we have seen, in consequence of the absence of intercellular spaces from veins of a certain order, the carbon dioxide transportation is strictly limited to definite areas, the size of which may be very different in different leaves. If these areas are minute we observe with the narrowest strips of darkening paper also the maximum width of the starch borders, the absolute dimensions of which are likewise minute.

This was the case in *Juglans*, *Aesculus* and *Tilia*, in which the distance of the transport could not be accurately determined, but certainly did not exceed 2—3 mm.

In *Dahlia* and in *Sambucus* the transport areas referred to are relatively very large, the starch borders along the narrowest strips of paper are narrowest, and they increase to a certain maximum width along the wider strips. Here, however, this method cannot give very accurate results. For if a transport area is darkened over its greater part, then much carbon dioxide is indeed formed in it, but this can only cause starch-formation in a small part. Conversely, if only a small part of the area is darkened, the starch-formation can be observed at a relatively large distance, but then too little carbon dioxide is formed in the small darkened portion to give rise to starch-formation in the more distant parts. With this reservation an experiment may be mentioned, which was made with the leaf of *Dahlia* (*Cactus*) *Thuringia* (exp. LX), with the result, that the carbon dioxide can here be carried over through at least 0.5 cm.

In summarizing his communication, the speaker points out that Mr. ZIJLSTRA has shown that transport of carbon dioxide is possible in all the leaves examined, and that it takes place through the intercellular spaces. The transport is completely dependent on the size and extent of these spaces in the leaf.

In some parallel-veined leaves, such as those of *Eichhornia*, *Pontederia* and *Eucomis*, the intercellular spaces are very wide and extend in an uninterrupted series throughout the whole length of the leaf. By the use of suitable apparatus the leaf base can be made to absorb carbon dioxide, which moving on through the intercellular spaces by diffusion can give rise to starch-formation a comparatively long way off in the leaf apex, when the latter is exposed to light.

In the great majority of leaves however, carbon dioxide transport cannot be shown with the relatively crude apparatus employed. In such leaves the carbon dioxide transport can be studied by another method, which utilizes the fact that respiratory carbon dioxide, which is formed in a darkened and shut off portion of the leaf, can diffuse from there through the intercellular spaces to neighbouring lighted portions of the leaf and can there cause starch-formation.

Such leaves possess limited transport areas, which are formed by spacious and connected intercellular spaces, and which are either connected at their margins through much narrower intercellular spaces, greatly retarding carbon dioxide transport (*Grasses*, *Acorus*, *Tradescantia*) or the areas are completely cut off by veins, which have no intercellular spaces (net-veined *Dicotyledonous* leaves). In these leaves with limited transport areas a carriage of carbon dioxide over a distance of from 2—3 mm. to at most 2.5 cm. is possible.

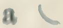
Finally the speaker draws special attention to the impossibility of carbon dioxide transport being of any advantage to the plant in nature, in the first place, because this transport is so extremely limited in the majority of cases, and in the second place especially because for transport it is necessary that the conducting part should not itself assimilate, and also, that the epidermis should be impervious to carbon dioxide. These conditions will doubtless never be fulfilled in land plants, in water plants perhaps very exceptionally.

It has therefore been established by Mr. ZIJLSTRA's investigations, that the speaker was wrong when, in his above cited paper, he came to the conclusion, that a leaf or leaf fragment cannot form starch in a space free from carbon dioxide, when parts organically connected with it, or even immediately adjoining it, are placed in an atmosphere very rich in carbon dioxide. Mr. ZIJLSTRA's results are however, in complete agreement with the main result, formerly obtained by the speaker, according to which the carbon dioxide of the soil, even if it should be absorbed by the roots, cannot appreciably contribute to the synthesis of organic matter in the leaf.

Groningen, January 29th, 1909.

Microbiology. — "*Investigations on the subject of disinfection*". By Prof. C. EIJKMAN.

Last year I communicated results of experiments [1]) from which it appeared that the resistance against high temperature of bacteria of the same pure culture is individually very different. While for example the majority die off in a few minutes, some may remain alive after $^1/_4$, $^1/_2$ hour, etc. If the times are noted on the absciss and the corresponding numbers of survivors are drawn to it as ordinates, we get as "curve of survivors" a line which in general has the form of a . In a slow process, as it occurs when the mortal temperature is taken relatively low, the first part of the curve shows itself clearly as an horizontal line and therefore represents a latent stage of incubation. Notwithstanding this the period within which the first half dies off, is much shorter than the following, in which the second half passes away.

In a quick process, as is observed when the temperature is far above the physiological limit, the duration of the incubation will become so brief that it easily escapes notice. In connection with the inevitable circumstance that the number of observations in this kind of experiments cannot be increased arbitrarily, but is confined within a rather definite period, the curve may, instead of the form, assume the shape of a .

The latter has also come to light in investigations published the other day by MADSEN & NYMAN, [2]) which differed from mine in so far as they were not made in vegetative forms of bacteria, but in (anthrax) spores and that the dying off for the greater part was not brought about by heat, but by a chemical means of disinfection, viz. sublimate.

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[1]) Biochem. Zeitschrift, Bnd. XI, Hft. 1—3, Festband Dr. H. J. HAMBURGER gewidmet.

[2]) Z. f. Hyg. u. Inf. Kr. Bnd. LVII.

The said investigators think that they are able to give a mathematical formula for their curve. They assert namely that the same formula is applicable here, which holds good for the so-called monomolecular reactions, e. g. for the inversion of cane-sugar by acid:

$$\frac{dx}{dt} = K(a-x).$$

In this formula a represents the number of living anthrax spores that was originally present, x the number that has died off after a space of time t, and K a constant, expressing the velocity of reaction, i. e. the velocity of disinfection. In other words this formula means that during the entire process the number dying off at any moment, is in a constant ratio to the number of living individuals present at that moment.

Therefore this K would yield a very suitable measure to judge about the action of a disinficiens under certain circumstances (of temperature, concentration, etc.). A much better measure than the one customary up till now, viz. the space of time necessary to destroy all germs. For it follows from what precedes that this space of time is to a high degree dependent on the number of germs which in the experiment has been started from. With this number the chance increases that there are some among them which offer resistance extremely long. On the other hand K is not to that degree dependent on the number of germs used in the experiment [1]) and in order to calculate it, the experiment need not even be continued till all germs have died off, but two determinations of x at arbitrary points of time would suffice.

For

$$K = \frac{1}{t_2 - t_1} \ln \frac{A - x_1}{A - x_2}$$ [2])

These experiences of Madsen and Nyman have been not only corroborated by an English investigator, Miss Harriett Chick [3]), for anthraxspores and sublimate, but she has stated a similar course of the curve also for the action of three disinfectants on vegetative forms of bacteria, only with this deviation that towards the end the velocity of reaction was decreasing, instead of remaining constant.

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[1]) Our experiences render it probable that a great number of germs per unit of volume somewhat retards the process of dying off.

[2]) See the text-books about physical chemistry.

[3]) Journal of Hygiene, 1908.

On the score of her experiments she is inclined to attribute this deviation to a difference in resistance between the individuals of various ages in the same culture. There would exist, as it were, an old and a young generation by the side of each other, the latter of which dies off slowest. Such a difference in connection with the age does not exist in spores to the same degree.

Of the curves published by me, it is, however, not only the tail, but also the head that shows a deviation. The course is here, still apart from the incubation, much slower than according to the formula. At the most the middle part is, stating roughly, in accordance with it.

Meanwhile it seems to me that this kind of investigations is hardly fit for a mathematical treatment.

Madsen & Nyman, for example, avail themselves of means, resulting from numbers of three values found, which deviate 25 °/₀ and more from these means.

An example from many [1]):

found:	193,	percentage of the average:	74.5
„	330,	„ „ „ „	127.4
„	254,	„ „ „ „	98.1
average:	259		100

And if the numerical results of Miss Chick are looked at somewhat more closely, they, too, do not appear to be more exact. Sometimes the errors in the observations are so great that, instead of the expected gradual decrease, here and there an increase of the number of survivors was in course of time to be noted [2]).

It may be called objectionable, as Madsen & Nyman do, to rid oneself of the deviations between the numbers determined experimentally and those calculated according to the formula, by remarking: "Wenn man die grossen Versuchsfehler, die an dieser Art von Untersuchungen kleben, in Betracht nimmt, ist die Uebereinstimmung eine recht gute". It is true, a line may be drawn between a number of points determined experimentally, leaving one point to the left, another again to the right, but when, as is not very seldom the case here, the deviations from the regularity are considerable, imagination and arbitrariness will get too large a scope to inspire confidence in the correctness of a curve construed in this way.

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[1]) l. c. Table XII.

[2]) l. c. Table III and X.

Seeing that my results did not well agree with those of the above investigators, and this difference might possibly be based upon the fact that the dying off of the microbes was brought about by heat and not by chemical means, I have extended the investigation in this direction. Again bacillus coli communis was made use of, a bacterium forming no spores, while as disinfectant was used phenol in a concentration of at most 1 °/₀, generally only ½ °/₀. The use of higher concentrations would make the process of dying off pass so quickly, that the time for a sufficient number of determinations would be too short, and among others the stage of incubation, if at all existing, would easily escape observation.

In order to have no great differences between the individuals and accordingly to render the conditions as little complicated as possible, as a rule a fresh (broth) culture, only a few hours old, incubated at 37°, was taken for the experiments, which culture, in its turn, had also been obtained by inoculation from a fresh culture. For the same reason the broth culture was slowly moved to and fro in a tube specially made for this purpose, which in an apparatus moved by a time-piece had been placed in the thermostate. Consequently all individuals were in well nigh equal conditions of development, so that the results of the experiments were more likely to be equivalent.

Before we used the culture for the experiment, it was centrifugalized in order to remove the clots of bacteria, which were probably to be found in it and for obvious reasons would have a disturbing effect. Besides it was strongly diluted (± 1000 times) with physiological common salt-solution. It would be necessary, in order to prevent sowing too many bacteria, to take of the non-diluted broth culture such small samples that, in measuring these, inevitably relatively too great mistakes would be made.

The vessel with the diluting fluid, provided with the necessary quantity of the disinfectant, had already beforehand got the required temperature in a waterbath with a toluolregulator and an automatic stirring-apparatus. After the inoculation with the broth culture the mixture was constantly kept in motion by a glass stirrer, in order to make the disinfectant work as equally as possible upon all germs.

As it is of great importance, to take the samples in rapid succession and just in time, I availed myself for this purpose of a peculiar kind of pipettes, which in case of immersion fill themselves automatically to the required height, so that the measuring, which takes up so much time, was avoided. The samples were put in Petri-scales and sown in melted, lightly alkaline reacting meat-agar. The development took place at 37°. The phenol put in the culture-plate together with the samples was bound by the alkali and, also because the the quantity was relatively small, it did not disturb the development of the colonies, as appeared from control experiments.

In the graphical representation of the results, to render a mutual comparison easier, a number of 1000 living germs has been started from and the values found experimentally have been reduced accordingly.

As proceeds from the figures, the type of the "curves of survivors" is in our disinfection-experiments with phenol quite similar to the one which was found in dying off by heat; very clearly the ⅂ form is again to be recognized in it.

Bac. coli

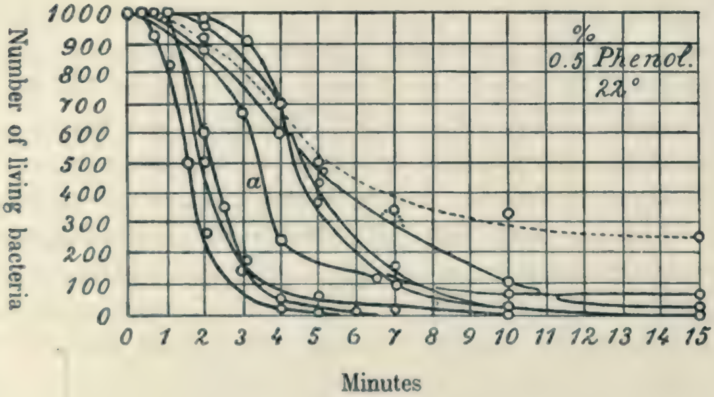

Fig. 1.

As in our experiments nothing has been left undone to put all the individualls, both in the process of incubation and that of disinfection, under quite the same conditions, a very marked accumulation of deaths might have been expected on either side of an average. In reality, however, this was not the case (most, though, with *a* in fig. 1) and again considerable differences of resistance between individuals of the same culture came to light. For this I see no other explanation, though it remains for the present only a mere supposition, than that the power of resistance during the development between two successive divisions undergoes changes. It may for example be imagined that under for the rest equal circumstances a daughter-cell just formed is, on account of her relatively larger surface, more vulnerable than a full-grown cell.

And because the length of generation is relatively short, amounting, in strong multiplication, to less than half an hour, all stages of development will occur by the side of each other.

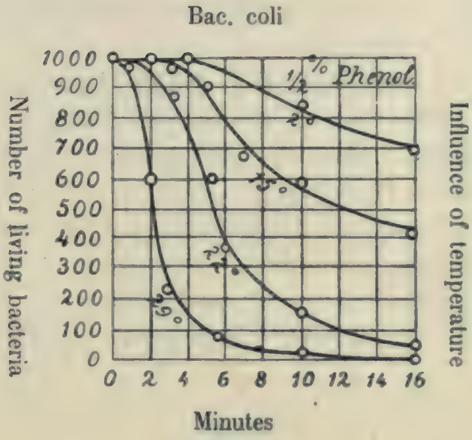

Fig. 2.

As in our former experiments, when the bacteria were killed by heat, we now also experienced, while using phenol as a disinfectant, that, though cultures of one stock are used at every time, yet we did not succeed in coming to somewhat equal results. This is taught by a look at fig. 1, in which a number of eight curves have been drawn, referring to experiments, made at different times each with fresh cultures of the same colistock. The concentration of the phenol and the temperature at which the disinfection took place, were in all cases the same and yet for the greater part quite different curves were obtained.

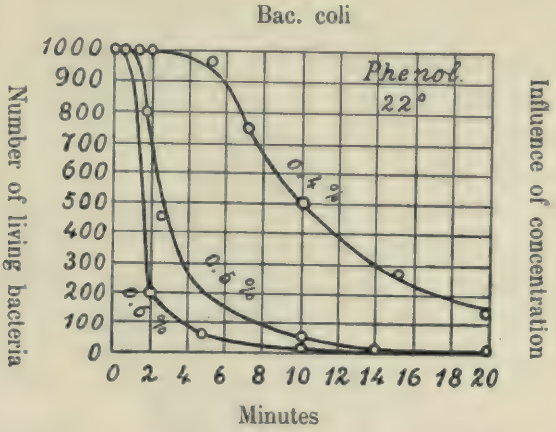

Fig. 3.

Owing to this, it will not do merely to compare the results of one experiment with those of another, unless both are made with the same culture and about the same time. Therefore strictly speaking parallel experiments are necessary, if one wishes to study the influence of some factor or other, as the concentration, the temperature, on the course of the process.

Madsen & Nyman and also Miss Chick derive from their observations that the influence of the above factors may likewise be expressed in formulas. Thus the well-known formula of Arrhenius in which the relation between temperature and velocity of reaction is expressed, would also hold good in this connection. It seems to me, for reasons already mentioned, to be prudent not to follow them on this path. Therefore we refer, with regard to the points meant, to the figures 2 and 3, without commenting on the subject.

Geology. — "*On a long-period Variation in the Height of the Ground-water in the Dunes of Holland.*" By Prof. Eug. Dubois. (Communicated by Dr. J. P. van der Stok).

Unmistakable and obvious is the lowering that the height of the ground-water in the dunes of the provinces of North- and South-Holland has undergone in consequence of the lowering of the level of the water at their east border (the making dry of the Lake of Harlem and of a large part of the IJ) and of deep cuttings in the dunes themselves (North-Sea Canal), furtheron, not less, by the collecting of large quantities of water supplies for some cities and towns.

From these causes there resulted a lowering which may be called a permanent one, inasmuch that soon they have brought about a new state of equilibrium with the supply by the part of rainfall which soaks in, and the flowing off. This really did take place in each case in which certain limits were not transgressed and as long as the collecting of water did not increase.

Side by side with these artificial changes of the height of the ground-water in the dunes, there exist also changes by natural, viz. climatal causes. These, in this as in other cases, are not continuous, but they do occur in periods. Indeed, in the latest historical past, as far as data are available, very clearly dry and wet epochs alternate with one another.

The Commission which, in 1891, inquired in the supplying of water from the dunes to Amsterdam pointed out, in their report, that from 1849 till 1856 there was a period of much rain, from 1856 till 1868 a dry period, again followed by the rainy years of 1869 till 1882. They showed also (for Utrecht) that under the combined influence of rainfall and evaporation such wet and dry epochs are found, with maxima about 1855—56 and 1882—1883 and a minimum about 1869—70.

In his "Hyetography of the Netherlands" Mr. ENGELENBURG [1]) inquires if there exists any relation between sunspots and rainfall. He finds that we can admit that such a relation, if it exists at all, does not appear very distinctly.

It is the merit of Dr. LAURENS VUYCK, in his elaborate treatise on the vegetation of the dunes, [2]) to have submitted the problem of the change of height of the ground-water in the dunes, as it also appears from older writings, to a close investigation. He however thinks of a progressive drying up of the low places in the dunes, having slowly taken place from as long ago as the end of the eighteenth century. From a careful consideration of the problem he arrives at the conclusion that the cause can only be found in a continuous and imperceptibly slow filling up of those low places with eolian sand.

The earliest intimation of the dunes drying out, which ought once more to be quoted, is from the end of the 18th century. In the report of a committee from that time to the Government, the reporter, JAN KOPS [3]) makes mention of the fact, that at the time of his inquiry, in 1797, the obstacle to the culture of the dunes arising from an excess of ground-water has been removed for a great deal. "In all our inspections, in the North as well as in the South, the most experienced people told us unanimously that during the last ten years, from year to year, less and less water than before is found in the plains amidst the dunes. They showed us places which formerly stood two or three feet under water and became extensive icefields for winter-sport, but now were only somewhat muddy in winter. In other plains, only four years ago, there stood still water in spring, from which nothing now is to be seen, and so it is with almost all the dunes. This particularity has raised our highest attention and surprise, as on account of the well known and alarming rising of the level of our rivers and inland water, we should expect the sinking down of the water of the dunes to be checked and prevented by it. Nobody was able to explicate to what cause this decrease of the dune-water should be imputed and we too could not trace out the true cause of it. But where it is to be sought for, this circumstance is most favourable for all following undertakings in the dunes." (p. 114 and 115).

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[1]) Physical Transactions of the Kon. Akad. v. Wet. Amsterdam 1891.

[2]) LAURENS VUYCK, De plantengroei der duinen, Leiden, 1898.

[3]) Rapport van de Commissie van Superintendentie over het onderzoek der Duinen van het voormaalig Hollandsch Gewest. Leiden 1798/99.

So it cannot astonish us that in 1805 A. P. TWENT [1]) makes mention of great dryness, making the birches in the plains amidst the dunes die at the tops, and that for three years there had been no water in places where in earlier times it always had been found, even in summer. "Considering that the sea does not be lower now than before, as shown by all circumstances, of which not the least certain is that the outlets of the inland waters are not improved in this part, this matter deserves double consideration by the naturalists".

In 1816 and still in 1823 a quite different state of things prevailed, as appears from the prize-essay on the making accessible of the valleys in the dunes along the coast of Holland by D. T. GEVERS, [2]) an answer to the question: where and how to drain the water from the plains in the dunes and at the same time facilitate the access to them, in order that they may no longer lie useless and uncultivated. This, namely, was imputed for the most part to the want of the necessary evacuation of the water. This inconvenience then was very great, and its removing indeed was the chief purpose of the large treatise.

Concerning a following dry period in the dunes no direct information has come to my knowledge. It appears however that from 1831 till 1840 the rainfall at Zwanenburg (Halfweg), that is very near the dunes, has been considerably below the average. [3])

Certainly the level of the ground-water in the dunes of the communes of Zandvoort, Bloemendaal and Velzen, as well as in the dunes of the province of South-Holland (cf. VUYCK, l. c. p. 184) was very high about 1845, so that for instance people skated in the dune-plains near Zandvoort.

On the contrary, about 1860, the ground-water in the dunes stood only little higher than in the present period which is get very dry; the water holes which contain now but little water were sufficiently but not abundantly provided. Though after 1858 the water supplies to Amsterdam, from the dunes, became less than in the former years and remained so till 1864, yet it was necessary to make new water collecting canals.

Then again follows a wet period, during which many plains and lower places in the dunes became marshy or were drowned in winter, frequented by a number of waterfowl (ducks, pool-snipes) and in some spots remained occupied by water even in summer, so that water-plants could flourish there. And such a state of things obtained in all the dunes, outside the influence of the large water works, arriving at a maximum about 1880.

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[1]) Wandeling naar de Zeeduinen van Wassenaar tot digt aan Scheveningen, p. 5.

[2]) D. T. GEVERS. Verhandeling over het toegangbaar maken van de duinvalleien langs de kust van Holland, uitgegeven door de Maatschappij ter bevordering van den Landbouw te Amsterdam opgerigt. Deel 18, Amsterdam 1826.

[3]) Nederlandsch Meteorologisch Jaarboek voor 1878, p. 288.

A few years later the present dry period commenced, by which, also independently of each artificial cause for a lowering of the ground-water in the dunes, its height decreased so much that in the present winter water is only found at 2 M. below the level surface of plains, which about 1880 were flooded in winter. Certainly no less than 2 to $2^1/_2$ M., in some places probably more, the ground-water is now lower, by natural causes alone, than it was in those wet years.

The periodical changes of the level of the ground-water in the dunes, thus appearing during more than a century, agree in striking conformity with the thirty-five-year period discovered by Prof. Ed. BRÜCKNER, according to which, in almost all the countries of the earth, the rainfall and the height of the water of lakes changes. Really between 1786 and 1805 a dry period occurs (for the Netherlands too this appears from the rainfall as determined at Zwanenburg). So in the beginning of the 19th century a minimum of rain and the lowest watermarks were reached. Then follows an epoch of much rain between 1806 and 1825, again a dry period from 1826 till 1840, a new period of much rain from 1841 till 1855, a dry period from 1856 till 1870, with a minimum about 1860, the latest period of much rain from 1871 till 1885, with a maximum about 1880, finally again a dry period, with a minimum about the end of the nineteenth century. A few years ago we still were in this dry half of the cycle.

Since, some years ago DR. WILLIAM J. S. LOCKYER [1]) proved, that in the amount of spotted area of the sun also, a thirty-five-year period could be traced, from 1833 till 1900, the discovery of BRÜCKNER surely has still gained in importance. On the other hand we now understand better what may be the cause of the few temporary or lasting deviations of some countries. If the better insight we now have got in the cause of the phenomenon discovered by BRÜCKNER is well adapted to increase our confidence that we have to count with it in future, we also need not suffer ourselves to be prevented from this by the deviations in question.

Lately, from the extensive study of the rainfall in Germany by Dr. G. HELLMANN [2]) and its discussion by BRÜCKNER [3]), it again appeared how in our vicinity wet and dry periods, and pretty well simultaneously with those in the dunes of Holland, alternate with one another.

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[1]) Proceedings of the Royal Society. Vol. 68. (1901). p. 285—300.

[2]) Die Niederschläge in den norddeutschen Stromgebieten. 3 Bände. Berlin, 1906.

[3]) Meteorologische Zeitschrift. Wien 1906, p. 565.

RAINFALL.

Millimeters					Progressive decadal sum above or below mean decadal sum over 50 years, percents.						
Year	Maestricht	Utrecht	Helder	Leiduin	Year	River basins of North Germany	Lower basin of the Rhine in Germany	Maestricht	Utrecht	Helder	Leiduin
1849		735.3									
1850		812.3									
1851		681.2									
1852		1048.[illegible]	876.0								
1853	489.7	737.5	662.9		53/54				3		
1854	687.9	821.1	715.2		54/55				2		
1855	543.6	6[illegible]0 9	478.2		55/56	—1	2		2		
1856	517.7	760.7	651.2		56/57	—2	1		1	—4	
1857	385.8	449.4	459.1		57/58	—3	—1	—12	—5	—7	
1858	417.1	634.9	637 1		58/59	—4	—1	—13	—8	—8	
1859	508.7	677.9	569.1		59/60	—7	—5	—18	—13	—12	
1860	628 5	810.8	730.7	874.8	60/61	—9	—6	—18	—12	—9	
1861	510 0	663.1	670.3	710 7	61/62	—8	—5	—15	—11	—4	
1862	566.2	590.8	6[illegible]0.5	659.0	62/63	—3	0	—9	—8	1	
1863	434.2	524.7	632.0	588.8	63/64	—1	2	—8	—7	0	
1864	363.3	459.7	448 0	551.2	64/65	—1	1	—6	—6	2	1
1865	549.5	710.2	696.4	822.2	65/66	—2	—1	—6	—7	3	2
1866	722.3	812.6	961.4	1065.5	66/67	—3	—1	—6	—7	2	2
1867	717.4	686 1	780.8	1047.7	67/68	—2	0	—6	—3	4	7
1868	513.3	674.4	602.4	7[illegible]5.6	68/69	—3	—1	—5	—2	4	10
1869	625.5	786.9	695.7	1013.0	69/70	—2	0	—3	2	7	14
1870	583.7	741.1	791.1	904.7	70/71	0	3	0	3	5	13
1871	504.3	640 1	603.2	764 0	71/72	—1	0	—1	2	2	11
1872	607.4	878.7	785.7	1075.5	72/73	—1	1	0	4	3	10
1873	505.8	576.3	628.1	803.9	73/74	0	3	3	5	6	12
1874	481 6	784.1	641.3	817.9	74/75	1	4	2	3	6	10
1875	724 4	787.4	565.1	808.2	75/76	3	6	2	4	2	8
1876	631.8	703.7	754.0	845.8	76/77	3	6	6	6	2	10
1877	746 6	826 1	845.4	986.8	77/78	6	8	9	7	5	10
1878	711.1	733.2	827.7	923.8	78/79	7	9	11	7	4	10
1879	561.3	698.0	664.5	803.1	79/80	8	9	12	5	4	8

RAINFALL

Millimeters					Progressive decadal sum above or below mean decadal sum over 50 years, percents.						
Year	Maestricht	Utrecht	Helder	Leiduin	Year	River basins of North Germany	Lower basin of the Rhine in Germany	Maestricht	Utrecht	Helder	Leiduin
1880	602.8	770.7	536.0	790.9	80/81	7	7	10	3	5	8
1881	730.2	773.2	627.4	913.9	81/82	7	7	7	3	5	8
1882	799.0	952.6	953.3	1029.5	82/83	4	4	5	—2	1	3
1883	624.6	618.0	601.9	841.0	83/84	4	3	4	—3	—2	0
1884	568.0	607.6	585.3	682.2	84/85	3	2	7	—1	—3	0
1885	560.1	633.3	656.4	805.4	85/86	1	0	9	—1	—2	0
1886	495.9	702.3	746.4	801.1	86/87	2	1	6	—1	—2	—1
1887	614.9	473.3	601.4	634.3	87/88	—2	—4	1	—3	—5	—2
1888	660.0	668.2	597.6	667.0	88/89	—2	—5	—1	—2	—3	—4
1889	742.8	874.1	639.4	834.4	89/90	—1	—4	0	0	0	—2
1890	701.7	777.7	606.0	743.7	90/91	—2	—4	2	1	1	—2
1891	522.3	788.3	587.1	854.2	91/92	—1	—4	2	1	—1	—4
1892	506.7	750.8	771.7	916.4	92/93	0	—4	1	5	0	—3
1893	542.7	711.9	702.3	710.4	93/94	—1	—6	—2	6	1	—1
1894	633.8	747.1	847.7	848.3	94/95	—1	—6	—6	3	1	—3
1895	668.2	743.1	678.2	772.7	95/96	—1	—6	—7	2	2	—3
1896	495.9	681.4	632.1	628.4	96/97			—8	3	2	—5
1897	553.9	733.0	658.2	794.5	97/98			—7	1	0	—8
1898	468.2	724.1	651.8	791.2	98/99			—5	4	3	—6
1899	527.5	691.0	637.0	633.8	99/1900			—7	2	—1	—8
1900	630.6	724.2	704.7	767.6	1900/01			—5	2	—3	—8
1901	467.0	817.6	608.8	730.1	01/02			—1	3	—2	—6
1902	527.8	631.3	604.9	659.0	02/03			0	2	—3	—8
1903	700.3	925.9	887.8	893.6	03/04			3	1	—5	—10
1904	481.0	596.1	580.3	660.1							
1905	782.4	776.0	579.5	777.6							
1906	772.5	723.9	654.1	808.4							
1907	596.7	659.7	607.3	632.3							
1908	630.6	643.8	539.2	629.9							
Av.	596.1	713.2	672.3	797.0							

In the accompanying table I tried to make clear the alternations of dry and wet periods of rainfall for some stations in the Netherlands, by the decadal sums, progressing from year to year, according to the method made use of by BRÜCKNER. In the first place we take Maestricht having the most continental situation of all the meteorological stations in the Netherlands with many years' determinations of rainfall, and being nearest to the basin area of the lower Rhine in Germany (Cleves, Bonn, Triers, Nancy), then Utrecht as intermediate between that station and Helder and Leiduin, which most of all the old stations may approach to the conditions obtaining in the dunes. The fifty-years' average rainfall of the three first-named Dutch stations is computed over 1859 till 1908, the average of Leiduin over 49 years only, beginning with 1860, the averages for Germany are over the years 1851 till 1900. The double years indicate the middle of each decade.

Now, what we observe is a close agreement and conformity to the rule of BRÜCKNER, generally, till 1882. In the last (dry) period, however, Helder and, in a still higher degree, Utrecht show important deviations. Maestricht, on the contrary, agrees very well and Leiduin tolerably with Germany and at the same time with by far the majority of all the countries of the world. Also after 1896, till 1900, also in the basin of the lower Rhine in Germany, just as at Maestricht, the rainfall remains considerably below the fifty-years average. About the beginning of the twentieth century the expected change took place every where. In the lower basin of the Rhine in Germany the rainfall in the years 1896 till 1900 exceeds the fifty-years' average by 4, 8, 10, 6 and 4 %, and in the latest lustrum the rainfall at Maestricht was nearly 10 % above the average, but not so at the three remaining stations, where deficits of 5, 11 and 12 % were observed, the wet period evidently not yet having commenced. On account however of the agreement with regular regions, during so long a time, as well as of the circumstance, that anticipation or retardation of an epoch is accustomed to be regained in the next period, the probability must not be called small, that for the whole of the Netherlands an epoch of increased rainfall and of higher ground-water levels is at hand, and that especially in the dunes too the ground-water will soon be rising.

Undoubtedly not only the annual rainfall, but also the evaporation is of consequence for that rising. But we know that evaporation is relatively small in periods of much rain and that, generally, the ground-water rises and falls with the amount of rainfall.

Variations in the rainfall are very strongly indicated by the height of the ground-water in the dunes. This not only is a consequence of this, that water enclosed in sand must rise three times as much as in an open basin, the supply being equal; but also of that circumstance, that the sand in question is particularly loose and composed of grains with equal dimensions, thus readily absorbing and giving way to the downfalling water. Further favourable conditions are that the ground is very uneven, not admitting of superficial flowing off, and only thinly covered with mosses, grasses, shrubs of *Hippophaë rhamnoïdes*, *Salix repens* and *Ligustrum vulgare* and with loose-crowned trees, especially birches. Really Mr. DE BRUYN found that, even during the dry years 1895 till 1902, at least half the rainfall served as a supply to the ground-water [1]). Moreover the geological constitution of the dune region, where eolian sand reposes upon the very little permeable fine clayey marine sands (Old Sea-clay and Sea-sand of STARING), favours very much the accumulation of the excess of rainfall.

The circumstance that so many low plains amidst the dunes, having subsisted during centuries, have undergone simultaneously quite the same up and down variations in the height of the ground-water, proves, as it seems to me, that we should not, generally, impute the becoming dry of the dunes to a successively filling up of those low places with eolian sand.

Another proof of no less strength I find in the phenomenon, already observed and rightly explained by GEVERS, that, on the whole, the surface line of the plains in the dunes runs parallel to the line of the ground-water, descending toward the sea and toward the polderland.

It is indeed unconceivable that those remarkably flat and pretty well horizontal, often very extensive low grounds amidst the dunes, commonly called in North-Holland "vlakken" and "velden", have had another origin than the sand being blown off — before the time that such blowing off was prevented by the planting of sand-binding grasses — till the level was reached where it was moistened by the ground-water, raised by capillarity to about thirty centimeters above its free level. Really we observe, as far as natural influences preponderate, that generally only where the character of the underground changes, making the water sink down accumulate in such places, in other places, these modifications in the geological structure modify the line of the ground-water, but at the same time, in consequence thereof, that of the surface of the dune plains.

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[1]) Handelingen van het 9de Natuur- en Geneeskundig Congres, 's-Gravenhage, 1903, p. 148.

Astronomy. — "*On the periodic solutions of a special case of the problem of four bodies*". By Prof. W. DE SITTER. (Communicated by Prof. E. F. VAN DE SANDE BAKHUYZEN).

The special case considered in this paper is that of a central body and three planets, or satellites, whose masses are small compared with the mass of the central body, and whose orbits are all situated in one and the same plane, the mean motions (in longitude) being *roughly* proportional to the numbers 4, 2 and 1. This special case is realised in nature by the three inner Galilean satellites of Jupiter, if the inclinations, the influence of the sun and of the fourth satellite, and the compression of the planet are neglected. This latter restriction is not essential, since the compression does not disturb the periodicity, provided only the motions take place exclusively in the plane of the planet's equator.

Neglecting at first the relation between the mean motions, we will consider the periodic solutions of the problem thus generalized for the case that the masses of the satellites are zero, i.e. for the unperturbed problem. These may be divided into two kinds, analogous to POINCARÉ's well known classification of the periodic solution of the problem of three bodies. In the solutions of the first kind (*sorte première* of POINCARÉ) the (unperturbed) orbits of the satellites are circles, in those of the second kind they are Keplerian ellipses with arbitrary excentricities.

The solutions of the first kind exist, if the *differences* of the mean motions are commensurable, thus:

$$\nu_1 - \nu_2 = p\nu, \qquad \nu_2 - \nu_3 = q\nu,$$

p and q being integers, mutually prime. This condition can also be expressed by saying that the mean motions must satisfy a linear equation of the form

$$\alpha\nu_1 + \beta\nu_2 + \gamma\nu_3 = 0,$$

where α, β and γ are mutually prime whole numbers, satisfying the relation

$$\alpha + \beta + \gamma = 0.$$

The mean motions can then be expressed thus:

$$\nu_1 = c_1\,\nu - \varkappa \qquad \nu_2 = c_2\,\nu - \varkappa \qquad \nu_3 = c_3\,\nu - \varkappa,$$

where c_1, c_2, c_3 are again whole numbers. We have then:

$$\alpha = c_2 - c_3 \qquad \beta = c_3 - c_1 \qquad \gamma = c_1 - c_2$$

$$p = c_1 - c_2 \qquad q = c_2 - c_3$$

Then, if we put

$$\nu t = \tau \qquad \varkappa t = v,$$

and if we count the time from the instant of a conjunction of II and III, and the longitudes from the common longitude of these satellites for that instant, we have

$$\lambda_3 = c_3\tau - v$$
$$\lambda_2 = c_2\tau - v$$
$$\lambda_1 = c_1\tau - v + K$$
$$\alpha\lambda_1 + \beta\lambda_2 + \gamma\lambda_3 = K.$$

After the lapse of the period

$$T = \frac{2\pi}{v}$$

the relative positions of the four bodies are the same as for the instant $t = 0$, the whole system being rotated in a retrograde direction through the angle $\varkappa T$.

By a reasoning entirely similar to that used by POINCARÉ[1]) for the solutions of the first kind of the problem of three bodies, we find easily that the condition, that these solutions shall remain periodic if the masses have small finite values, is

$$K = 0^\circ \text{ or } 180^\circ.$$

In other words, there must be a symmetrical conjunction or opposition of the three satellites at the beginning of the period.[2])

The reasoning by which the existence of these solutions for small values of the masses is proved, fails in only one case, viz. when

$$\frac{\varkappa}{\nu} = 0 \text{ or a whole number.}$$

This exceptional case is analogous to the well known exceptional case for the periodic solutions of the first kind of the problem of three bodies.

For the special case of Jupiter's satellites we have

$$\alpha = 1,\ \beta = -3,\ \gamma = 2,\ K = 180^\circ$$
$$\lambda_1 = 4\tau - v + 180^\circ$$
$$\lambda_2 = 2\tau - v$$
$$\lambda_3 = \tau - v$$
$$\tau = \lambda_2 - \lambda_3 \qquad v = \lambda_2 - 2\,\lambda_3$$

In the system of Jupiter we find that ν is small compared with τ. We have roughly (in degrees per day):

$$v = 51^\circ.0571$$
$$\varkappa = 0\ .7395.$$

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[1]) *Les méthodes nouvelles de la mécanique céleste*, tome I, § 40.

[2]) See also *Les méthodes nouvelles*, t. I. § 50.

It is owing to this particular circumstance, that the motion of the satellites can also be considered as a periodic solution of the second kind, as will now be shown.

In the periodic solutions of the second kind of the unperturbed problem the excentricities are arbitrary, and the mean motions (not only their differences) are mutually commensurable. In other words we have here $\varkappa = 0$.

If the masses are not zero, these solutions may also remain periodic. In the perturbed motion we must then distinguish the mean motions in *longitude* and those in *anomaly*. Let

$$l_i = n_i t + l_{io} \text{ be the mean anomaly}$$

$$\lambda_i = \nu_i t + \lambda_{i} \quad \text{,, \quad ,, \quad ,, longitude,}$$

if then π_i be the longitude of the pericentre, we have

$$\lambda_i = l_i + \pi_i$$

$$\nu_i = n_i + \frac{d\pi_i}{dt} \qquad n_i = c_i \nu$$

Inquiring into the conditions that these solutions shall remain periodic for small finite values of the masses, we find again that there must be a symmetrical conjunction at the beginning of the period, i. e. for $t = 0$. The angles

$$\pi_{10} - \pi_{20} \qquad \pi_{20} - \pi_{30}$$

$$l_{10} \qquad l_{20} \qquad l_{30}$$

must all be 0° or 180°. One of the angles l_{io} (e.g. l_{30}) can always be made identically zero (or 180°) by a convenient choice of the zero epoch. There thus remain 4 angles, each of which can have one of two values. We have thus 16 combinations which may *a priori* be expected to give rise to periodic solutions.

Now if $\frac{d\pi_i}{dt}$ were zero, then at the end of the period $T = \frac{2\pi}{\nu}$ the configuration for $t = 0$ would be exactly restored, as it is in the unperturbed problem. It is, however, sufficient to insure the periodicity of the solution, that the value of $\frac{d\pi_i}{dt}$ integrated over a complete period shall be the same for the three satellites. In addition to the conditions of symmetry we have therefore the conditions

$$\int_0^T \frac{d\pi_1}{dt}\, dt = \int_0^T \frac{d\pi_2}{dt}\, dt = \int_0^T \frac{d\pi_3}{dt}\, dt = -\varkappa T \quad . \quad . \quad (1)$$

After the completion of the period the whole system is then rotated through the angle $-\varkappa T$, as in the solutions of the first kind.

The mean motions in *longitude* are the same as in the solutions of the first kind, viz.:

$$\nu_i = c_i \nu - \varkappa,$$

The mean motions in *anomaly* remain rigorously commensurable.[1])

I will now restrict the discussion to the special case represented in the system of Jupiter, viz.:

$$c_1 = 4 \;,\; c_2 = 2 \;,\; c_3 = 1.$$

For the general case similar results will be found, which I do not however at present propose to investigate.

Moreover I will limit myself to the consideration of small excentricities, which is the only case that is of immediate practical value. Whether the conditions (1) do also admit solutions with large excentricities, is a question which can only be answered by a special investigation.

Under these restrictions we find that out of the 16 combinations satisfying the conditions of symmetry, there are only 4 which also satisfy the conditions (1). For two of these $\varkappa$ is positive, and for the two others it is negative. Further, if the quantity

$$\lambda_1 - 3\,\lambda_2 + 2\,\lambda_3 = K$$

is formed for each of these solutions, it will be found that one of the solutions with a positive $\varkappa$ has $K = 0°$ and the other has $K = 180°$, and similarly for the solutions with a negative $\varkappa$. Of these four solutions that with $K = 180°$ and $\varkappa$ positive (the case of nature) is the only stable one.

These solutions of the second kind thus appear, on both sides of the exceptional point $\varkappa = 0$, as the natural continuations of the two possible solutions of the first kind ($K = 0°$ and $K = 180°$). In the solutions of the first kind the unperturbed orbit is circular, the perturbed orbit is affected by a "great inequality", with the argument $c_i \tau$. In the solutions of the second kind this inequality appears as an equation of the centre [2]). In the solutions of the first kind we have the condition that the unperturbed excentricity must be zero; corresponding to this the excentricities in the solutions of the second kind are not arbitrary, but must be determined from the equations (1). When the value of $\varkappa$ is the same for both cases, the two solutions are entirely equivalent.

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[1]) These solutions are based on the same principle as those investigated by SCHWARZSCHILD (Astr. Nachr. 3506). SCHWARZSCHILD, however, only considers the case of two planets, one of which has an excentricity, and at the same time an infinitely small mass. Consequently the orbit of the other planet, which is a circle, is not perturbed.

[2]) In the integration by the usual method, this inequality presents itself as a perturbation of the excentricities and pericentres.

Besides this "great" inequality there are, of course, a number of others, whose arguments are multiples of τ, which are the same in the two solutions.

In order now to investigate these solutions according to the theory of POINCARÉ, we must write down the conditions of periodicity

$$\psi_i = \int_0^T \frac{dE_i}{dt}\, dt = 0$$

where for E_i we must take successively each of the elements of the system. If further β_i be the small correction to be applied to the value of E_i (for $t = 0$) in the unperturbed orbit, in order to retain the periodicity in the perturbed orbit, then the stability of the solution depends on the roots of the equation

$$\Delta(s) = \begin{vmatrix} \frac{\partial\psi_1}{\partial\beta_1} + 1 - s & \frac{\partial\psi_1}{\partial\beta_2} \cdots\cdots & \frac{\partial\psi_1}{\partial\beta_n} \\ \frac{\partial\psi_2}{\partial\beta_1} & \frac{\partial\psi_2}{\partial\beta_2} + 1 - s \cdots & \frac{\partial\psi_2}{\partial\beta_n} \\ \vdots & \vdots & \vdots \\ \frac{\partial\psi_n}{\partial\beta_1} & \frac{\partial\psi_n}{\partial\beta_2} \cdots & \frac{\partial\psi_n}{\partial\beta_n} + 1 - s \end{vmatrix} = 0 \quad \ldots \quad (2)$$

If we put $s = e^{\alpha T}$ (or, approximately, $1 - s = -\alpha T$), then the condition that the orbit shall be stable, is that all the values of α^2 are real and negative (with the exception of one or more, which may be identically zero).

I will introduce the elements

$$L_i, \quad \Pi_i, \quad l_i, \quad \pi_i,$$

of which the meaning is

$$L_i = m_i \sqrt{a_i} \qquad \Pi_i = L_i \sqrt{1 - e_i^2}$$

l_i = mean anomaly

π_i = longitude of pericentre.

Supposing the units to be so chosen that the constant of GAUSS and the mass of the central body are unity, the equations of motion are:

$$\frac{dL_i}{dt} = -\frac{\partial F}{\partial l_i} \qquad \frac{d\Pi_i}{dt} = -\frac{\partial F}{\partial \pi_i}$$

$$\frac{dl_i}{dt} = \frac{\partial F}{\partial L_i} \qquad \frac{d\pi_i}{dt} = \frac{\partial F}{\partial \Pi_i}$$

$$F = F_0 - R$$

$$F_0 = -\frac{m_1^3}{2L_1^2} - \frac{m_2^3}{2L_2^2} - \frac{m_3^3}{2L_3^2}$$

In the unperturbed motion we have

$$l_i = n_i\,t + l_{i0}\,, \qquad n_i = \frac{m_i^3}{L_i^3} = \frac{1}{a_i^{3/2}},$$

and the constants a_i must be such, that

$$n_1 = 4\,\nu \qquad n_2 = 2\,\nu \qquad n_3 = \nu.$$

The integral of areas is

$$\Phi = \Pi_1 + \Pi_2 + \Pi_3 = \text{const.}$$

By means of this integral we can eliminate Π_3, and diminish the number of degrees of freedom by one. For this purpose we introduce

$$G_1 = \Pi_1 \qquad G_2 = \Pi_2$$

$$g_1 = \pi_1 - \pi_3 \qquad g_2 = \pi_2 - \pi_3$$

The equations then preserve the canonic form. [1])

In forming the equations $\psi_i = 0$ we need only those terms of R, whose integral over a complete period does not vanish, i.e. those in whose arguments the mean anomalies do either not occur, or occur only in the combinations

$$l = l_1 - 2\,l_2 \qquad l' = l_2 - 2\,l_3,$$

of which the mean motions are zero. The constant term will not be required in what follows. Of the others, we only require the terms of the lowest degree in the excentricities. Thus, introducing the further notations

$$\pi_1 - \pi_2 = g_1 - g_2 = \omega$$

$$\pi_2 - \pi_3 = \quad g_2 \quad = \omega',$$

we find that R can be replaced by

$$R' = \frac{m_1\,m_2}{a_2}\left\{-A\,\varepsilon_1 \cos(l + 2\omega) + B\varepsilon_2 \cos(l + \omega)\right\} +$$

$$+ \frac{m_2\,m_3}{a_3}\left\{-A\varepsilon_2 \cos(l' + 2\omega') + B\varepsilon_3 \cos(l' + \omega')\right\} \quad . \quad . \quad . \quad (3)$$

where

$$A = a'\,(4\,A^{(2)} + A_1^{(2)})$$

$$B = a'\,(3\,A^{(1)} + A_1^{(1)} - \frac{2}{\sqrt{aa'}}),$$

The symbols $A_p^{(i)}$ have the usual meaning (Leverrier, Annales de Paris, tome 1, p. 260, 262), and must be computed for the value

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[1]) The integral of areas still exists, if the compression of the planet is taken into account, provided only the motion takes place in the plane of the equator. Also those terms of the perturbing function which are here used, remain the same. The conclusions reached below, thus can be applied unaltered to the case of a compressed planet.

$$\frac{a}{a'} = \left(\frac{n_2}{n_1}\right)^{2/3} = \left(\frac{n_3}{n_2}\right)^{2/3} = \left(\frac{1}{2}\right)^{2/3} = 0.630.$$

The coefficients A and B then are pure numbers. Their values are

$$A = +\,2.381$$
$$B = +\,0.964.$$

The meaning of the symbols ε_i occurring in R' is

$$\varepsilon_i = \sqrt{\frac{L_i - \Pi_i}{2\,L_i}} = \sin \frac{1}{2}\,\varphi_i\,,$$

or approximately

$$\varepsilon_i = \frac{1}{2}\,e_i$$

The expressions of the various differential coefficients of R' are:

$$\frac{\partial R'}{\partial L_i} = \frac{2\sqrt{a_i}}{m_i}\,\frac{\partial R'}{\partial a_i} + \frac{\cos\varphi_i}{4\,m_i\sqrt{a_i}}\,\frac{1}{\varepsilon_i}\,\frac{\partial R'}{\partial \varepsilon_i}$$

$$\frac{\partial R'}{\partial \Pi_i} = \frac{1}{4\,m_i\,\sqrt{a_i}}\,\frac{1}{\varepsilon_i}\,\frac{\partial R'}{\partial \varepsilon_i}$$

$$\frac{\partial R'}{\partial G_1} = \frac{\partial R'}{\partial \Pi_1} - \frac{\partial R'}{\partial \Pi_2} \qquad \frac{\partial R'}{\partial G_2} = \frac{\partial R'}{\partial \Pi_3} - \frac{\partial R'}{\partial \Pi_2}$$

$$\frac{\partial R'}{dl_1} = \frac{\partial R'}{dl} \qquad \frac{\partial R'}{\partial l_2} = -\,2\,\frac{\partial R'}{dl} + \frac{\partial R'}{\partial l'} \qquad \frac{\partial R'}{\partial l_3} = -\,2\,\frac{\partial R'}{\partial l'}$$

$$\frac{\partial R'}{\partial g_1} = \frac{\partial R'}{d\omega} \qquad \frac{\partial R'}{\partial g_2} = -\,\frac{\partial R'}{\partial \omega} + \frac{\partial R'}{\partial \omega'}.$$

The quantities β_i and ψ_i will be supposed to be correlated to the different elements as follows:

To:	L_1	L_2	L_3	G_1	G_2	l_1	l_2	l_3	g_1	g_2
correspond:	β_1	β_2	β_3	β_4	β_5	β_6	β_7	β_8	β_9	β_{10}
and:	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	ψ_6	ψ_7	ψ_8	ψ_9	ψ_{10}.

If in R' and its differential coefficients the elements are replaced by their unperturbed values, these funtions become constant. Consequently the first terms of the developments of the functions ψ_i in powers of the masses are of the form

$$\int_0^T D\,dt = T\,.\,D,$$

where D represents a differential coefficient of R' in which, after the differentiation, the unperturbed values of the elements have been substituted.

Now we have

$$\frac{dL_i}{dt}=\frac{\partial R'_i}{\partial l_i} \quad , \quad \frac{dG_i}{dt}=\frac{\partial R'_i}{\partial g_i}.$$

The functions $\psi_1 , \psi_2 , \psi_3 , \psi_4$ and ψ_5 therefore contain only sines of linear combinations of the angles l, l', ω, ω'. Further we have

$$4\,\frac{\partial R'}{\partial l_1}+2\,\frac{\partial R'}{\partial l_2}+\frac{\partial R'}{\partial l_3}=0\,,$$

and therefore the equation $\psi_1=0$ is a necessary consequence of $\psi_2=0$ and $\psi_3=0$. The four remaining mutually independent equations

$$\psi_2=\psi_3=\psi_4=\psi_5=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

correspond to what has in the beginning of this paper been called the "conditions of symmetry". If we put

$$l_0=(l_1-2\,l_2)_0=\alpha \qquad l'_0=(l_2-2\,l_3)_0=\alpha'$$
$$\omega_0=(\pi_1-\pi_2)_0=\beta \qquad \omega'_0=(\pi_2-\pi_3)_0=\beta',$$

(the subscript 0 indicating the unperturbed value, or the average value over a complete period in the periodic solution), then the equations (4) are satisfied, if each of the angles

$$\alpha\ ,\ \alpha'\ ,\ \beta\ ,\ \beta'$$

is either 0° or 180°.

These conditions being satisfied, we can, in the differential coefficients of R' (after the differentation) replace the angles l, l', ω, ω' by $\alpha, \alpha', \beta, \beta'$.

The developments of the functions $\psi_1 , \ . \ . \ . \ \psi_5$ in powers of β_i are

$$\psi_1=T\left\{\beta_6\,\frac{\partial^2 R'}{\partial l_1{}^2}+\beta_7\,\frac{\partial^2 R'}{\partial l_1 \partial l_2}+\ldots+\beta_{10}\,\frac{\partial^2 R'}{\partial l_1 \partial g_3}\right\}+\begin{array}{c}\text{terms of}\\ \text{higher orders}\end{array}$$

and similar formulae for ψ_2, ψ_3, ψ_4 and ψ_5. Then we find easily

$$\psi_6=T\,\beta_1\,\frac{\partial^2 F_0}{\partial L_1{}^2}+\ \text{terms of higher order,}$$

and similarly ψ_7 and ψ_8. These equations give $\beta_1=\beta_2=\beta_3=0$, in other words the mean motions in *anomaly* (n_i) are not changed. Finally we have

$$\psi_9=-\int_0^T\frac{\partial R'}{\partial G_1}\,dt=-\,T\,\frac{\partial R'}{\partial \Pi_1}+T\,\frac{\partial R'}{\partial \Pi_2}$$

$$\psi_{10}=-\,T\,\frac{\partial R'}{\partial \Pi_2}+T\,\frac{\partial R'}{\partial \Pi_3}$$

The equations $\psi_9=\psi_{10}=0$ are thus found to represent the conditions (1), since

$$\int_0^T \frac{d\pi_i}{dt}\,dt = -T\,\frac{\partial R'}{\partial \Pi_i}$$

From the value (3) of R' we find easily (remembering that $a_i^{-3/2} = n_i = c_i\nu$ ($c_1 = 4$, $c_2 = 2$, $c_3 = 1$) and $\nu T = 2\pi$)

$$\Omega_1 = \frac{1}{2\pi}\int_0^T \frac{d\pi_1}{dt}\,dt = -\,m_2\,\frac{a_1}{a_2}\,\frac{A}{\varepsilon_1}\cos\alpha,$$

$$\Omega_2 = \frac{1}{2\pi}\int_0^T \frac{d\pi_2}{dt}\,dt = \frac{1}{2}\left\{ m_1\,\frac{B}{\varepsilon_2}\cos(\alpha+\beta) - m_3\,\frac{a_2}{a_3}\,\frac{A}{\varepsilon_2}\cos\alpha' \right\},$$

$$\Omega_3 = \frac{1}{2\pi}\int_0^T \frac{d\pi_3}{dt}\,dt = \frac{1}{4}\,m_2\,\frac{B}{\varepsilon_3}\cos(\alpha'+\beta').$$

The conditions (1) can thus be written

$$\Omega_1 = \Omega_2 = \Omega_3 = -\,\frac{\varkappa T}{2\pi} = -\,\frac{\varkappa}{\nu}.$$

Collecting now the 16 different possible combinations of values

	α	β	α'	β'	Ω_1	Ω_2	Ω_3	
(1)	0 °	0 °	0 °	0 °	—	O	+	*impossible.*
(2)	0	0	0	180	—	O	—	conditional.
(3)	0	0	180	0	—	+	—	*impossible.*
(4)	0	0	180	180	—	+	+	*impossible.*
(5)	0	180	0	0	—	—	+	*impossible.*
(6)	0	180	0	180	—	—	—	**possible.**
(7)	0	180	180	0	—	O	—	conditional.
(8)	0	180	180	180	—	O	+	*impossible.*
(9)	180	0	0	0	+	—	+	*impossible.*
(10)	180	0	0	180	+	—	—	*impossible.*
(11)	180	0	180	0	+	O	—	*impossible.*
(12)	180	0	180	180	+	O	+	conditional.
(13)	180	180	0	0	+	O	+	conditional.
(14)	180	180	0	180	+	O	—	*impossible.*
(15)	180	180	180	0	+	+	—	*impossible.*
(16)	180	180	180	180	+	+	+	**possible.**

of α, α', β and β', we find the following summary. Only those combinations can give rise to periodic solutions, in which Ω_1, Ω_2 and Ω_3 are of the same sign. The letter O stands for *undetermined.*

Out of these 16 combinations there are only two, (6) and (16), for which the perturbed orbit can remain periodic for all values of the masses. There are four: (2), (7), (12) and (13), for which the periodicity is only possible if a certain condition involving the masses is satisfied.

For all solutions we find from the equation $\psi_9 = 0$

$$\frac{\varepsilon_1}{\varepsilon_3} = 4\,\frac{a_1\,A}{a_2\,B} = 6.225.$$

It needs hardly be pointed out, that this is only a rough approximation, the higher orders of ε_i having been neglected. In the system of Jupiter's satellites we find actually (see these Proceedings, March 1909 [1])) $\varepsilon_1/\varepsilon_3 = 6.77$.

Further if we put

$$\frac{m_1}{m_2} = \mu_1 \qquad\qquad \frac{m_3}{m_2} = \mu_3$$

$$P = \mu_3\,\frac{a_2}{a_3}\,A + \mu_1\,B,$$

then we find, for the solutions (6) and (16), from $\psi_{10} = 0$

$$\frac{\varepsilon_3}{\varepsilon_2} = 2\,\frac{P}{B} \qquad\qquad \frac{\varepsilon_3}{\varepsilon_1} = \frac{1}{2}\,\frac{a_2}{a_1}\,\frac{P}{A}.$$

If the longitudes are counted from the apocentre of III, and the time from a passage of III through this apocentre, we have, for $t = 0$, $\pi_3 = 180^\circ$, $l_3 = 180^\circ$, therefore $\lambda_3 = 0^\circ$. For the corresponding values for II and I we find, for $t = 0$, for solution (6):

$$\begin{array}{ll} \pi_2 = 0^\circ & \qquad\pi_1 = 180^\circ \\ l_2 = 0 & \qquad l_1 = 0 \\ \lambda_2 = 0 & \qquad\lambda_1 = 180 \end{array}$$

$$K = \lambda_1 - 3\lambda_2 + 2\lambda_3 = 180^\circ$$

and $\varkappa$ is *positive*: the mean motion in anomaly exceeds the mean motion in longitude. This is the case of nature.

For the solution (16) we find:

$$\begin{array}{ll} \pi_2 = \quad 0^\circ & \qquad\pi_1 = 180^\circ \\ l_2 = 180 & \qquad l_1 = 180 \\ \lambda_2 = 180 & \qquad\lambda_1 = \quad 0 \\ K = 180^\circ & \qquad\varkappa \textit{ negative.} \end{array}$$

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[1]) The expressions there given are based on SOUILLART's theory. The quantities ε_i, which here appear as excentricities, are thus there considered as perturbations, and are called x_1, x_2, x_3.

The possibility of the solutions (2), (7), (12) and (13) depends on the sign of Ω_2. In all these cases $cos(\alpha + \beta)$ and $cos\,\alpha'$ are of the same sign. Thus if we put

$$Q = \mu_3 \frac{a_2}{a_3} A - \mu_1 B,$$

we find that for positive values of Q the solutions (2) and (12) can exist, (7) and (13) being impossible; for negative values of Q (2) and (12) become impossible, but (7) and (13) are possible. We find for these solutions:

$$\begin{array}{cc} \text{Solution (2)} & \\ \pi_2 = 0^\circ & \pi_1 = 0^\circ \\ l_2 = 0 & l_1 = 0 \\ \lambda_2 = 0 & \lambda_1 = 0 \\ \multicolumn{2}{c}{\varkappa \textit{ positive.}} \end{array} \qquad \begin{array}{cc} \text{Solution (12)} & \\ \pi_2 = 0^\circ & \pi_1 = 0^\circ \\ l_2 = 180 & l_1 = 180 \\ \lambda_2 = 180 & \lambda_1 = 180 \\ \multicolumn{2}{c}{\varkappa \textit{ negative.}} \end{array}$$

$$\begin{array}{cc} \text{Solution (7)} & \\ \pi_2 = 180^\circ & \pi_1 = 0^\circ \\ l_2 = 180 & l_1 = 0 \\ \lambda_2 = 0 & \lambda_1 = 0 \\ \multicolumn{2}{c}{\varkappa \textit{ positive.}} \end{array} \qquad \begin{array}{cc} \text{Solution (13)} & \\ \pi_2 = 180^\circ & \pi_1 = 0^\circ \\ l_2 = 0 & l_1 = 180 \\ \lambda_2 = 180 & \lambda_1 = 180 \\ \multicolumn{2}{c}{\varkappa \textit{ negative.}} \end{array}$$

All four solutions have $K = 0^\circ$.

For the solutions (2) and (12) we find

$$\frac{\varepsilon_2}{\varepsilon_3} = 2\frac{Q}{B} \qquad \frac{\varepsilon_2}{\varepsilon_1} = \frac{1}{2}\frac{a_2}{a_1}\frac{Q}{A}$$

and for (7) and (13)

$$\frac{\varepsilon_2}{\varepsilon_3} = -2\frac{Q}{B} \qquad \frac{\varepsilon_2}{\varepsilon_1} = -\frac{1}{2}\frac{a_2}{a_1}\frac{Q}{A}.$$

For $Q = 0$ (or, if higher orders of ε_i are taken into account, for a value of $\frac{\mu_1}{\mu_3}$ in the neighbourhood of the value for which $Q = 0$) we have $\varepsilon_2 = 0$. The solutions (2) and (7) then become identical, and similarly (12) and (13). We thus find that the two cases (2) and (7) form together one continuous family, which exists for all values of $\frac{m_1}{m_3}$. The same thing is true of (12) and (13).

Thus all that has been said above regarding the existence of the periodic solutions has now been proved. It remains to investigate their stability. For that purpose we must form the equation (2). We introduce the notations:

$$\frac{1-s}{T\sqrt{m_3}} = -\varrho, \qquad \frac{1}{m_3^2}\frac{\partial^2 R'}{\partial x \partial y} = (xy), \qquad m_3 \frac{\partial^2 R'}{\partial p \partial q} = [pq],$$

where x and y represent two of the variables l_i, g_i and p and q two of the variables L_i, G_i. The quantities (xy) are of the order zero in the masses, the quantities $[pq]$ are of the first order.

With the aid of the values of ψ_i, which have been derived above, it is now easy to write down the determinant $\Delta(s)$. The differential coefficients such as $\frac{\partial \psi_6}{\partial \beta_1} = \frac{\partial^2 F_0}{\partial L_1^2}$ will have m_2 in the denominator. To remove this, and to make all terms of the same type also of the same order in the masses, the five lower rows have been multiplied by m_2. Then the five upper rows, have been divided by $\sqrt{m_2}$, and the last five columns by $m_2 \sqrt{m_2}$. Finally every term has been divided by T. The equation then becomes

$$\begin{vmatrix}
-\rho & 0 & 0 & 0 & 0 & (l_1 l_1) & (l_1 l_2) & (l_1 l_3) & (l_1 g_1) & (l_1 g_2) \\
0 & -\rho & 0 & 0 & 0 & (l_1 l_2) & (l_2 l_2) & (l_2 l_3) & (l_2 g_1) & (l_2 g_2) \\
0 & 0 & -\rho & 0 & 0 & (l_1 l_3) & (l_2 l_3) & (l_3 l_3) & (l_3 g_1) & (l_3 g_2) \\
0 & 0 & 0 & -\rho & 0 & (l_1 g_1) & (l_2 g_1) & (l_3 g_1) & (g_1 g_1) & (g_1 g_2) \\
0 & 0 & 0 & 0 & -\rho & (l_1 g_2) & (l_2 g_2) & (l_3 g_2) & (g_1 g_2) & (g_2 g_2) \\
K_1-[L_1 L_1] & -[L_1 L_2] & -[L_1 L_3] & -[L_1 G_1] & -[L_1 G_2] & -\rho & 0 & 0 & 0 & 0 \\
-[L_1 L_2] & K_2-[L_2 L_2] & -[L_2 L_3] & -[L_2 G_1] & -[L_2 G_2] & 0 & -\rho & 0 & 0 & 0 \\
-[L_1 L_3] & -[L_2 L_3] & K_3-[L_3 L_3] & -[L_3 G_1] & -[L_3 G_2] & 0 & 0 & -\rho & 0 & 0 \\
-[L_1 G_1] & -[L_2 G_1] & -[L_3 G_1] & -[G_1 G_1] & -[G_1 G_2] & 0 & 0 & 0 & -\rho & 0 \\
-[L_1 G_2] & -[L_2 G_2] & -[L_3 G_2] & -[G_1 G_2] & -[G_2 G_2] & 0 & 0 & 0 & 0 & -\rho
\end{vmatrix} = 0, \quad (5$$

For brevity we have put

$$K_1 = -\frac{3}{\mu_1 a_1^2}, \quad K_2 = -\frac{3}{a_2^2}, \quad K_3 = -\frac{3}{\mu_3 a_3^2}.$$

To simplify the determinant (5), we may use the relation, which has already been mentioned above,

$$4\,(l_1\, x) + 2\,(l_2\, x) + (l_3\, x) = 0,$$

where x represents an arbitrary element. We perform the following operations, which are here, in order to save space, only indicated (the ordinary figures refer to the columns, the roman figures to the rows):

To (8) add 4.(6) + 2.(7), From (*VI*) subtract 4.(*VIII*)
„ (*VII*) „ 2.(*VIII*),
„ (*III*) „ 4 (*I*) + 2.(*II*), „ (1) „ 4.(3),
„ (2) „ 2.(3).

The determinant then becomes divisible by ϱ^2, and the columns (3) and (8) and the rows (III) and (VIII) drop out. For the sake of clearness I will, however, continue to indicate the remaining columns by their original rotation-numbers.

Now we have[1])

$$\begin{aligned}
(l_1 l_1) &= (ll), & (g_1 g_1) &= (\omega\omega),\\
(l_1 l_2) &= -\,2(ll), & (g_1 g_2) &= -\,(\omega\omega),\\
(l_2 l_2) &= 4(ll) + (l'l'), & (g_2 g_2) &= (\omega\omega) + (\omega'\omega'),\\
(l_1 g_1) &= (l\omega), & (l_1 g_2) &= -\,(l\omega),\\
(l_2 g_1) &= -\,2(l\omega), & (l_2 g_2) &= 2(l\omega) + (l'\omega').
\end{aligned}$$

By means of these relations the determinant can be still further simplified. We perform the following operations

To (7) add 2.(6), From (VI) subtract 2.(VII)
„ (II) „ 2.(I), „ (1) „ 2.(2)
„ (10) „ (9), „ (IX) „ (X)
„ (V) „ (IV), „ (4) „ (5).

If now the remaining rows and columns are rearranged in the following order

$$\begin{array}{cccccccc}
1, & 2, & 6, & 7, & 4, & 5, & 9, & 10,\\
\mathrm{I}, & \mathrm{II}, & \mathrm{VI}, & \mathrm{VII}, & \mathrm{IV}, & \mathrm{V}, & \mathrm{IX}, & \mathrm{X},
\end{array}$$

then the equation becomes

$$\Delta(\varrho) = \begin{vmatrix}
-\varrho & 0 & (ll) & 0 & 0 & 0 & (l\omega) & 0\\
0 & -\varrho & 0 & (l'l') & 0 & 0 & 0 & (l'\omega')\\
A_{11} & A_{12} & -\varrho & 0 & A_{13} & A_{14} & 0 & 0\\
A_{21} & A_{22} & 0 & -\varrho & A_{23} & A_{24} & 0 & 0\\
0 & 0 & (l\omega) & 0 & -\varrho & 0 & (\omega\omega) & 0\\
0 & 0 & 0 & (l'\omega') & 0 & -\varrho & 0 & (\omega'\omega')\\
A_{31} & A_{32} & 0 & 0 & A_{33} & A_{34} & -\varrho & 0\\
A_{41} & A_{42} & 0 & 0 & A_{43} & A_{44} & 0 & -\varrho
\end{vmatrix} = 0, \quad . \quad (6)$$

where the meaning of the coefficients is as follows (I mention only those coefficients that will be used below, those omitted all contain m_3 as a factor):

$$\begin{aligned}
A_{11} &= K_1 + 4\,K_2 \quad + \text{ terms of higher orders}\\
A_{12} &= A_{21} = -\,2\,K_2 + \quad \text{„ „ „ „}\\
A_{22} &= K_2 + 4\,K_3 \quad + \quad \text{„ „ „ „}\\
A_{33} &= -\,[G_1G_1] + 2\,[G_1G_2] - [G_2G_2]\\
A_{34} &= A_{43} = -\,[G_1G_2] + [G_2G_2]\\
A_{44} &= -\,[G_2G_2]
\end{aligned}$$

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[1]) These formulas suppose $(ll') = (\omega\omega') = (l'\omega) = (l\omega') = 0$. This is only true if the *third* and higher orders of e are neglected.

The expressions $[pq]$ all contain m_2 as a factor. Thus, in order to derive the term independent of m_2 in the development of ϱ, we take all those expressions $= 0$. The determinant then becomes divisible by ϱ^4, and is reduced to its first four columns and rows. Four of the eight roots of our equation thus appear to be divisible by $\sqrt{m_2}$. The first terms of the other four are the roots of the equation:

$$\begin{vmatrix} -\varrho & 0 & s & 0 \\ 0 & -\varrho & 0 & s' \\ A_{11} & A_{12} & -\varrho & 0 \\ A_{21} & A_{22} & 0 & -\varrho \end{vmatrix} = 0,$$

or

$$\varrho^4 - (A_{11}\, s + A_{22}\, s')\, \varrho^2 + (A_{11}\, A_{22} - A^2_{12})\, ss' = 0\,, \quad . \quad . \quad . \quad (7)$$

where we have put, for brevity:

$$(ll) = s\,, \quad (l'l') = s'.$$

The solution can only be stable, if the equation (7) has two real and negative roots. Now A_{11} and A_{22} are negative, and $A_{11}\, A_{22} - A^2_{12}$ is positive. The necessary and sufficient condition that the equation (7) shall have two real and negative roots is therefore, that both *s and s'* are *positive*. Now we have

$$\left.\begin{aligned} s &= \frac{\mu_1}{a_2} \left\{ A\, \varepsilon_1 \cos \alpha - B\, \varepsilon_2 \cos(\alpha + \beta) \right\} \\ s' &= \frac{\mu_3}{a_2} \left\{ A\, \varepsilon_3 \cos \alpha' - B\, \varepsilon_2 \cos(\alpha' + \beta') \right\} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (8)$$

For the six possible combinations we find the signs of s and s' as given below

	α	β	α'	β'	s	s'	
(6)	0°	180°	0°	180°	+	+	
(16)	180	180	180	180	—	—	*unstable.*
(2)	0	0	0	180	0	+	
(7)	0	180	180	0	+	0	
(12)	180	0	180	180	0	—	*unstable.*
(13)	180	180	0	0	—	0	*unstable.*

The solutions (16), (12) and (13), i.e. those with a negative value of $\varkappa$, are thus certainly unstable. For (2) s will be positive if

$$A\,\varepsilon_1 - B\,\varepsilon_2 > 0.$$

By using the value of $\frac{\varepsilon_2}{\varepsilon_1}$ found above, this leads to the condition

$$Q < 2\,\frac{a_1}{a_2}\,\frac{A^2}{B} = 7.41.$$

Similarly we find for (7) that s' will be positive if

$$Q > -\frac{1}{2}\,\frac{B^2}{A} = -\,0.46.$$

For the family consisting of the solutions (2) and (7) we thus find that s and s' are both positive for all values of Q between the limits $-\,0.46$ and $+\,7.41$. For the Jovian system we find $Q = +\,4.14$.

For the solution (6) both s and s' are always positive.

This is, however, not sufficient to prove the stability of these solutions. We must also consider the four remaining roots of our equation (6). To determine these I divide the last two rows and the 5th and 6th columns of that determinant by $\sqrt{m_2}$. Introducing then

$$\varrho = \varrho'\sqrt{m_2}\,, \qquad A_{ij} = m_2\,B_{ij}\,,$$

the equation becomes

$$\Delta\,(\rho') = \begin{vmatrix}
-\rho'\sqrt{m_2} & 0 & (ll) & 0 & 0 & 0 & (l\omega) & 0 \\
0 & -\rho'\sqrt{m_2} & 0 & (l'l') & 0 & 0 & 0 & (l'\omega') \\
A_{11} & A_{12} & -\rho'\sqrt{m_2} & 0 & B_{13}\sqrt{m_2} & B_{14}\sqrt{m_2} & 0 & 0 \\
A_{21} & A_{22} & 0 & -\rho'\sqrt{m_2} & B_{23}\sqrt{m_2} & B_{24}\sqrt{m_2} & 0 & 0 \\
0 & 0 & (l\omega) & 0 & -\rho' & 0 & (\omega\omega) & 0 \\
0 & 0 & 0 & (l'\omega') & 0 & -\rho' & 0 & (\omega'\omega') \\
B_{31}\sqrt{m_2} & B_{32}\sqrt{m_2} & 0 & 0 & B_{33} & B_{34} & -\rho' & 0 \\
B_{41}\sqrt{m_2} & B_{42}\sqrt{m_2} & 0 & 0 & B_{43} & B_{44} & 0 & -\rho'
\end{vmatrix} = 0.$$

If now again we neglect all terms which appear multiplied by $\sqrt{m_2}$, and if we perform the operations

From (7) subtract $\frac{(l\omega)}{(ll)}\,.\,(3)$, from (8) subtract $\frac{(l'\omega')}{(l'l')}\,.\,(4)$,

we find

$$\Delta\,(\varrho') = \begin{vmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{vmatrix} . \, ss' \, . \begin{vmatrix}
-\varrho' & 0 & \sigma & 0 \\
0 & -\varrho' & 0 & \sigma' \\
B_{33} & B_{34} & -\varrho' & 0 \\
B_{43} & B_{44} & 0 & -\varrho'
\end{vmatrix} = 0,$$

where we have put

$$\sigma = (\omega\omega) - \frac{(l\omega)^2}{(ll)}, \quad \sigma' = (\omega'\omega') - \frac{(l'\omega')^2}{(l'l')}.$$

We thus find that ϱ' is determined by an equation very similar to (7). For the coefficients B_{ij} we find easily

$$B_{33} = H_1 + H_2,$$
$$B_{34} = B_{43} = -H_2,$$
$$B_{44} = H_2 + H_3,$$

where

$$H_1 = -\frac{\partial^2 R'}{\partial \Pi^2_1} = -\frac{1}{16}\frac{1}{\mu_1 a_1 a_2}\frac{A}{\varepsilon^3_1} \cos \alpha,$$

$$H_2 = -\frac{\partial^2 R'}{\partial \Pi^2_2} = \frac{1}{16}\left\{\frac{\mu_1}{a^2_2}\frac{B}{\varepsilon^3_2}\cos(\alpha + \beta) - \frac{\mu_3}{a_2 a_3}\frac{A}{\varepsilon^3_2}\cos \alpha'\right\},$$

$$H_3 = -\frac{\partial^2 R'}{\partial \Pi^2_3} = \frac{1}{16}\frac{1}{\mu_3 a^2_3}\frac{B}{\varepsilon^3_3}\cos(\alpha' + \beta').$$

For the cases (6), (2) and (7), which are the only ones that we need investigate, all these expressions are negative. For H_1 and H_3 this is at once evident. For H_2 we find:

	Sol. (6)	Sol. (2)	Sol. (7)
$H_2 =$	$-\dfrac{P}{16a^2_2\varepsilon^3_2}$,	$-\dfrac{Q}{16a^2_2\varepsilon^3_2}$,	$\dfrac{Q}{16a^2_2\varepsilon^3_2}$,

which is also negative in all three cases. The equation determining the first term of ϱ' now becomes

$$\varrho'^4 - \{(H_1 + H_2)\sigma + (H_2 + H_3)\sigma'\}\varrho'^2 + \{H_1.H_2 + H_1.H_3 + H_2.H_3\}\sigma\sigma' = 0, \quad . \text{(9)}$$

The condition that this equation shall have two real and negative roots is again that σ and σ' are both positive. Now we have

$$\sigma = (\omega\omega) - \frac{(l\omega)^2}{s}, \qquad \sigma' = (\omega'\omega') - \frac{(l'\omega')^2}{s'}.$$

It is only necessary to investigate those cases where s and s' are both positive. The conditions of stability thus become

$$s.(\omega\omega) > (l\omega)^2, \qquad s'.(\omega'\omega') > (l'\omega')^2.$$

The values of s and s' have already been given above (8). For the other quantities we find

$$(\omega\omega) = \frac{\mu_1}{a_2} \left\{ 4\, A\, \varepsilon_1 \cos \alpha - B\, \varepsilon_2 \cos (\alpha + \beta) \right\},$$

$$(\omega'\omega') = \frac{\mu_2}{a_3} \left\{ 4\, A\, \varepsilon_2 \cos \alpha' - B\, \varepsilon_3 \cos (\alpha' + \beta') \right\},$$

$$(\,l\, \omega\,) = \frac{\mu_1}{a_2} \left\{ 2\, A\, \varepsilon_1 \cos \alpha - B\, \varepsilon_2 \cos (\alpha + \beta) \right\},$$

$$(l'\, \omega') = \frac{\mu_2}{a_3} \left\{ 2\, A\, \varepsilon_2 \cos \alpha' - B\, \varepsilon_3 \cos (\alpha' + \beta') \right\},$$

from which

$$s.\ (\omega\,\omega) = \frac{\mu_1{}^2}{a_2{}^2} \left\{ 4\, A^2\, \varepsilon_1{}^2 + B^2\, \varepsilon_2{}^2 - 5\, A\, B\, \varepsilon_1\, \varepsilon_2 \cos \beta \right\},$$

$$(\,l\omega\,)^2 = \frac{\mu_1{}^2}{a_2{}^2} \left\{ 4\, A^2\, \varepsilon_1{}^2 + B^2\, \varepsilon_2{}^2 - 4\, A\, B\, \varepsilon_1\, \varepsilon_2 \cos \beta \right\}.$$

Therefore

$$s.\ \sigma = - \frac{\mu^2{}_1}{a^2{}_2} A\, B\, \varepsilon_1\, \varepsilon_2 \cos \beta,$$

and similarly

$$s'.\ \sigma' = - \frac{\mu_2{}^2}{a_3{}^2} A\, B\, \varepsilon_2\, \varepsilon_3 \cos \beta'$$

The only stable solutions are thus those in which β and β' are both 180°, and the only solution which satisfies this condition is (6). This solution, i. e. the case actually occurring in nature, is thus found to be the *only* stable periodic solution.

It needs hardly be mentioned that all the proofs given above suppose, that the developments in powers of ε_i and m_i converge so rapidly, that the sign of the various quantities used is determined by their first term. What the upper limits of ε_i and m_i are satisfying this condition, cannot be stated without a special investigation, but nature teaches us, that for the values occurring in the system of Jupiter the solution (6) still exists as a stable solution.

Physics. — "*Contribution to the theory of binary mixtures*, XIII." By Prof. J. D. VAN DER WAALS.

We have considered the closed curve, discussed in the preceding Contributions, as the projection of the section of two surfaces, viz. $\frac{d^2\psi}{dx^2} = 0$, and $\frac{d^2\psi}{dv^2} = 0$, constructed on an x-axis, a v-axis and a T-axis. Let the x-axis be directed to the right, the v-axis to the front and the T-axis vertically. The projection of these sections on the other projection planes will now also be a closed curve, in general with a continuous course. We shall here chiefly consider the projection on the T,x-plane. This projection will possess a lowest and a highest point, and be enclosed on the right and on the left between a minimum and a maximum value of x, which two values of x are the same as those between which the v,x-projection is enclosed. But the highest and the lowest point of the T,x-projection is no special point in the v,x-projection. Only in this v,x-projection the points mentioned have the property that a line $\frac{d^2\psi}{dv^2}=0$ and also a line $\frac{d^2\psi}{dx^2}=0$ touches this v,x-projection at the minimum or the maximum temperature. At all temperatures between this minimum and this maximum temperature the v,x-projection is intersected by a line $\frac{d^2\psi}{dv^2}=0$ in two points, and also by a line $\frac{d^2\psi}{dx^2}=0$. But this contact can take place e. g. for the minimum temperature in a point that lies either on the left or on the right of the point in which v has the minimum value, and even, but in special cases, exactly in that point. So the quantity $\frac{dv}{dx}$ can be both positive and negative for the point in which T is maximum.

This holds also for the point where T is maximum, but generally the first mentioned point is of greater importance.

If for this first-mentioned point $\frac{dv}{dx}$ is positive, this is also the case with $\frac{dv}{dx}$ for the point in which $\frac{d^2\psi}{dv^2}=0$ touches the closed curve, and as $\frac{d^3\psi}{dv^2dx}+\frac{d^3\psi}{dv^3}\frac{dv}{dx}=0$, the quantity $\frac{d^3\psi}{dv^2dx}$ will be negative in the point in which T is minimum. In the same way the quantity $\frac{d^3\psi}{dx^3}$ is positive, and $\frac{d^2p}{dx^2}$ is positive for that point because also the line $\frac{d^2\psi}{dx^2}=0$ touches, and so $\frac{d^3\psi}{dx^3}+\frac{d^3\psi}{dx^2dv}\frac{dv}{dx}=0$, and the contact takes place in such a way that the whole closed curve lies inside $\frac{d^2\psi}{dx^2}=0$. If the minimum temperature should just happen to be in the point of the closed curve where $\frac{dv}{dx}=0$, we have at the same time

$\frac{d^2p}{dxdv} = 0$ and $\frac{d^2\psi}{dx^2} = 0$. If, on the other hand $\frac{dv}{dx}$ is negative, $\frac{d^2p}{dx\,dv}$ is negative and also $\frac{d^2\psi}{dx^2}$.

If the whole curve has contracted to a single point, this applies also to the two other projections — and for this case it is easy to express these projections in the value of ε_1 and ε_2 and n. Then, as was found before, $x = \frac{\sqrt{\varepsilon_1}}{n-1}$, and $1-x = \frac{n\sqrt{\varepsilon_2}}{n-1}$. Then the value of $\frac{v}{b}$ is equal to $\frac{1}{1-A}$ or equal to $1+B$, or $\frac{v}{b} = 1 + \frac{(n-1)^2}{n} \frac{\sqrt{\varepsilon_1}\sqrt{\varepsilon_2}}{(\sqrt{\varepsilon_1}+\sqrt{\varepsilon_2})^2}$ or $\frac{v-b}{b} = \frac{(n-1)^2}{n} \frac{\sqrt{\varepsilon_1}\sqrt{\varepsilon_2}}{(\sqrt{\varepsilon_1}+\sqrt{\varepsilon_2})^2}$. Both for $\varepsilon_1 = 0$ and for $\varepsilon_2 = 0$ is $v - b = 0$, and as we have to do with a point lying on the line $\frac{dp}{dv} = 0$, $T = 0$. A maximum value of v does not occur, but a maximum value of $\frac{v}{b}$ does. The easiest way to find this is by retaining the form:

$$\frac{v}{b} = 1 + B = 1 + \frac{(n-1)^2\,x\,(1-x)}{(1-x+nx)^2}.$$

If v could be maximum, then:

$$\frac{\frac{db}{dx}}{b} + \frac{\frac{dB}{dx}}{1+B} = 0$$

or

$$\frac{n-1}{1+(n-1)x} + \frac{(n-1)^2\,\frac{(1-x)^2-n^2x^2}{[1+(n-1)x]^4}}{1+\frac{(n-1)^2x(1-x)}{[1+(n-1)x]^2}} = 0.$$

After reduction we should find $n = 0$. But the maximum value of $\frac{v}{b}$ or of $\frac{dB}{dx} = 0$ requires $nx = 1 - x$ or $x = \frac{1}{n+1}$.

If for x and $1-x$ we put the value $\sqrt{\varepsilon_1}$ and $n\sqrt{\varepsilon_2}$, we find as condition $\varepsilon_1 = \varepsilon_2$, and so $p_{k_1} = p_{k_2}$. Then the value of $\frac{v}{b}$ is equal to $1 + \frac{(n-1)^2}{4n} = \frac{(n+1)^2}{4n}$. When n is small, $\frac{v}{b}$ is only little greater than 1, and so T much smaller than T_k. But for very high values of n, e. g. about 10, the critical volume can be reached, and so T

can be $= T_k$. With constantly rising value of n, the quantity $\frac{v}{b}$ can, indeed, increase indefinitely, in which, however, T becomes an ever smaller fraction of T_k. The value, however, which ε_1 and ε_2 will have, and consequently the value of x, $\frac{v}{b}$, and T, cannot be chosen arbitrarily. Besides that ε_1 and ε_2 must have such a value that the point denoted by them, lies on the parabola OPQ, the condition must also be fulfilled that $a^2_{12} = l^2 a_1 a_2$. For the case that $l^2 = 1$, the values of ε_1 and ε_2 are easy to calculate. Then the point $(\varepsilon_1, \varepsilon_2)$ must also lie on a second parabola, congruent with PQO, and shifted by an amount 1 along the ε_1 and ε_2-axis in negative direction. These parabolae having their axes parallel, there will only be a single point of intersection. The equations which are to be satisfied, are then:

$$(\varepsilon_1 - n^2 \varepsilon_2)^2 = 4\, n' (n - 1)(\varepsilon_1 - n\, \varepsilon_2)$$

and

$$(\varepsilon_1 - n^2 \varepsilon_2 + n^2 - 1)^2 = 4\, n\, (n - 1)(\varepsilon_1 - n\, \varepsilon_2 + n - 1).$$

Then we find:

$$\sqrt{\varepsilon_1} = \frac{n+3}{4(n+1)}(n - 1)$$

and

$$n \sqrt{\varepsilon_2} = \frac{3n+1}{4(n+1)}(n - 1),$$

or $x = \frac{n+3}{4(n+1)}$ and $1 - x = \frac{3n+1}{4(n+1)}$. The value of T obtained in this case is smaller than the one calculated above if we take $\varepsilon_1 = \varepsilon_2$. If $l^2 < 1$, ε_1 increases, of course, and ε_2 decreases and reversely. A value of l^2 might be chosen so that T assumes a maximum value, but to this we come back later on. But in any case the values of ε_1 and ε_2 may be such that the two surfaces $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2}$ touch only at one single temperature, without intersecting further. And if n is not very large, this temperature lies very low. Thus from the formula $MRT = 2\frac{a}{b}\frac{\left(\frac{v-b}{b}\right)^2}{\left(\frac{v}{b}\right)^3}$ and the supposition $l^2 = 1$ we calculate for $n = 2$ the value of $\frac{T}{T_k} = \frac{1}{14}$ about, and for other values of l^2 this value of $\frac{T}{T_k}$ becomes but little higher. But ε_1 and ε_2 might be such for higher value of n, that v approaches to $3b$ and T to T_k; this might be the case for $n = 10$. So we see here the following possibilities for the phenomena of non-miscibility, dependent on the value of n. For low value of n, contact of the said two surfaces may take place at so low a temperature that observation is impossible on account of the occurrence of the solid state. For increasing value of n this temperature rises, and for a certain value of n, it may have risen to $^1/_3$ or $^1/_2$ T_k and so the observation will no longer be prevented by the appearance of the solid state. As, if contact takes place of the two surfaces at certain temperature, two plaitpoints make their appearance already at lower temperature, which vanish again at higher temperature than that of the contact, three-phase-pressure will exist between two temperatures. A precise determination of the value of n at which this is the case, is not possible, if it were only on account of the fact that we have not been able to determine what relation exists between the temperature of contact and that at which the double plaitpoint begins to appear or disappears, and moreover because we have not been able to determine how long the double plaitpoint must have been present before the plaitpoint appears or disappears on the binodal line. But for small value of n the lowest temperature at which non-miscibility sets in, can certainly not be observed, at least not if the cause of non-miscibility is to be ascribed to the circumstance discussed here.

So in the T,x-projection there is only a single point for which the value of x will be found in the left half, in the case discussed here. But if we besides draw the T,x-projection of the plaitpoints which are the consequence of the existence of the point of contact of $\frac{d^2\psi}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$, we obtain again a closed curve. Probably the projection of the point of contact lies, especially as regards the value of x, very eccentrically with regard to this curve — possibly even to the right outside it. The lefthand branch of this curve is the projection of the irrealisable plaitpoints, and these will always have considerably moved to smaller values of x. But if the projection is a closed curve, they must rapidly approach the points of the righthand branch at higher temperature. However, another case may be expected. In the case that the projection of the plaitpoints remains below the curve indicating the course of T_k, the closed curve is to be expected — but if the value of T should rise so high that the curve $T_k = f(x)$ would be cut, the lefthand branch of the projection would meet the ordinary plaitpoint, which approaches from the side of the component with the lowest value of T_l. The result is then that the projection of the plaitpoints forms a curve which begins at $x=0$ and $T=T_{k_1}$, rises from there to the highest double plaitpoint temperature, then falls to the lowest plaitpoint temperature, and ascends again from there to T_{k_2}. This last case has been treated more extensively These Proc. Vol. VII. The transformation of a branch plait etc.

Figure 39 gives a schematic representation of the T,x-projection for the first case. The point P represents the point of contact of the two surfaces $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}=0$. The full line represents the locus of the plaitpoints, the point P_{ab} is the lowest double plaitpoint, and P_{cd} is the highest. In the points Q_1 and Q_2 the realisable plaitpoint appears or disappears on the binodal line — and then there is three-phase-pressure between the temperatures of Q_1 and Q_2. The dotted curve, which has its lowest and its highest

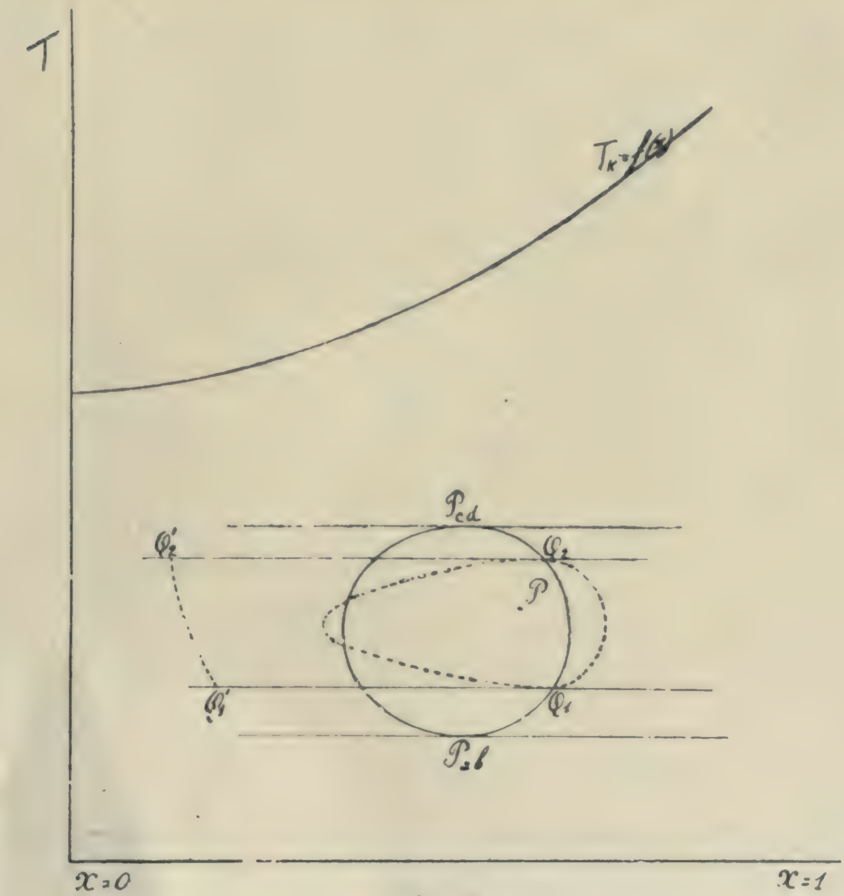

Fig. 39

point in Q_1 and Q_2, denotes the concentrations of the coexisting liquid phases at every T, and the curve Q'_1, Q'_2 indicates the concentration of the third coexisting phase (vapour phase). The curve $T_k = f(x)$ has been drawn higher in the figure.

It follows, however, from the remark, Contribution XI, p. 440, Vol. XI, that the point P need not even be present, and that yet the remaining part of the figure, but then between narrower temperature limits, may continue to exist. We might even imagine the circumstances to be such that the points P_{ab} and P_{cd} coincide, but then Q_1 and Q_2 and Q'_1 and Q'_2 would have coincided already before.

The second case is represented in fig. 40. Again P is the projection on the T,x-plane of the point of contact of the two surfaces $\frac{d\psi^2}{dx^2} = 0$ and $\frac{d^2\psi}{dv^2} = 0$ The full curve $A\ Q_2\ P_{cd}\ P_{ab}\ Q_1\ B$ etc. is that of the plaitpoints. The points P_{ab} and P_{cd} are the double plaitpoints. So

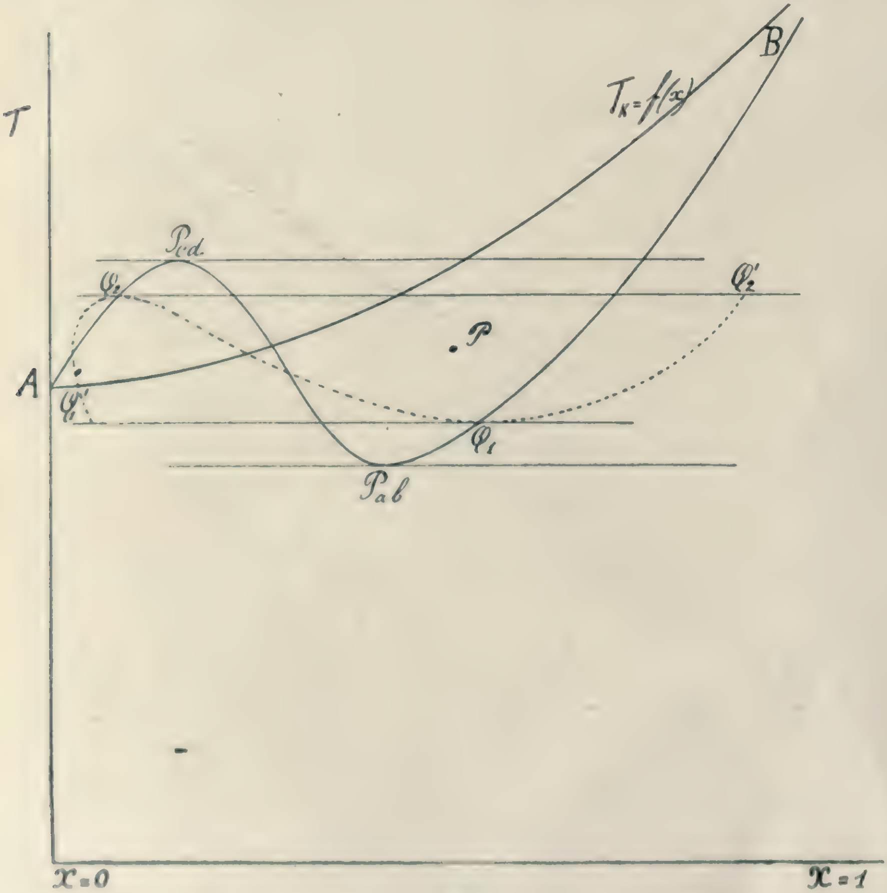

Fig. 40.

there are three plaitpoints between the temperature of A, viz. T_{k_1}, and that of P_{cd}, unless P_{ab} should lie higher than A, in which case P_{ab} would take the place of T_{k_1}. The curve $T_k = f(x)$ is also inserted in the figure. It will have to intersect the plaitpoint curve at $x < 1$, and that twice. The first point has not been indicated by a special mark, but the second point of intersection is supposed to be in the neighbourhood of B. If we draw a p,x-section of the surface of saturation, and add to it a line indicating the pressure at which there would be coexistence if the mixture behaved as an homogeneous substance, the extreme point of this line would lie at the same value of x as that of the plaitpoint, at the value of T of the second point of intersection just mentioned.

For higher value of T we have then again the rule that for a given mixture $T_{pl} > T_k$, which is generally considered as the normal case. This being really the case for x very small, and x nearly 1, when there is intersection of the curves $T_k = f(x)$ and $T_{pl} = \varphi(x)$, this will have to take place twice. For the points Q_1 and Q_2 the plaitpoint lies on the binodal line, and between the temperatures Q_1 and Q_2 there is three-phase-pressure. The concentration of the three coexisting phases is indicated by the dotted line $Q'_1 Q_2 Q_1 Q'_2$. We might call the part $Q'_1 Q_2$ of this line the vapour branch. The vapour branch presents a particularity in the drawing which has escaped attention so far, viz. that it can contain a point in which x has a minimum value. I have not drawn this particularity in the vapour branch of fig. 39, because it is less probable there. This applying to a circumstance which has not been noticed as yet, and which is yet not devoid of importance, a digression to show the possibility of the existence of such a point with minimum value of x, may be useful. The more so, because in the discussion properties will be mentioned the knowledge of which is necessary if we want to understand the full meaning of different particularities occurring for the three-phase-pressure.

Let us call the concentration of the point representing the vapour phase, x_1, and let x_2 and x_3 denote the concentrations of the liquid phase — and let us put $x_1 < x_2 < x_3$. Now the following equations hold:

$$v_{21}\, dp = (x_2 - x_1)\left(\frac{d^2\zeta}{dx_1^{\,2}}\right)_{pT} dx_1 + \eta_{21}\, dT$$

and

$$v_{31}\, dp = (x_3 - x_1)\left(\frac{d^2\zeta}{dx_1^{\,2}}\right)_{pT} dx_1 + \eta_{31}\, dT.$$

For the three-phase-pressure both equations hold, and we get the value of $\frac{dp}{dT}$ for this three-phase-pressure which we shall indicate by $\frac{dp}{dT_{123}}$, by eliminating dx_1 from these two equations. If we divide the first equations by $x_2 - x_1$, and the second by $x_3 - x_1$, and if we subtract the quotients from each other, we get the well-known formula:

$$\frac{dp}{dT_{123}} = \frac{\frac{\eta_2 - \eta_1}{x_2 - x_1} - \frac{\eta_3 - \eta_1}{x_3 - x_1}}{\frac{v_2 - v_1}{x_2 - x_1} - \frac{v_3 - v_1}{x_3 - x_1}}.$$

If we substitute this value of $\frac{dp}{dT_{123}}$ in the two equations given we get:

$$v_{21} \frac{dp}{dT_{123}} = (x_2 - x_1)\left(\frac{d^2\zeta}{dx_1^2}\right)_{pT} \frac{dx_1}{dT} + \eta_{21}$$

and

$$v_{31} \frac{dp}{dT_{123}} = (x_3 - x_1)\left(\frac{d_{21}\zeta}{dx_1^2}\right)_{pT} \frac{dx_1}{dT} + \eta_{31}.$$

After division by v_{21} and v_{31} we may also write:

$$\frac{dp}{dT_{123}} = \frac{\left(\frac{d^2\zeta}{dx_1^2}\right)_{pT} \frac{dx_1}{dT}}{\frac{v_{21}}{x_2 - x_1}} + \left(\frac{\partial p}{\partial T}\right)_{x_{21}}$$

and

$$\frac{dp}{dT_{123}} = \frac{\left(\frac{d^{31}\zeta}{dx_1^2}\right)_{pT} \frac{dx_3}{dT}}{\frac{v_{31}}{x_3 - x_1}} + \left(\frac{\partial p}{\partial T}\right)_{x_{31}},$$

or

$$\frac{dp}{dT_{123}} = \left(\frac{dp}{dx_1}\right)_T \frac{dx_1}{dT} + \left(\frac{\partial p}{\partial T}\right)_{x_{31}}$$

if we represent by $\left(\frac{dp}{dT}\right)_{x_{21}}$ and $\left(\frac{dp}{dT}\right)_{x_{31}}$ the ratio of the increase of p and the increase of T on the vapour sheet of the surface of saturation for a section with constant value of $x = x_1$, respectively for the coexisting equilibrium between the phases 1 with 2, and 1 with 3. So the difference $\frac{dp}{dT_{123}} - \left(\frac{dp}{dT}\right)_{x_{21}}$, multiplied by $\frac{v_{21}}{x_2 - x_1}$

indicates the sign of dx_1. In the same way if we change 2 into 3. Now it is true that the surface of saturation has been greatly modified by the existence of the three-phase-pressure. But this modification is restricted to values of T, between those at which this pressure begins and ends, and also within these limits of temperature, the surface of saturation consists only of a lower sheet and an upper sheet, if we leave the metastable and unstable coexisting phases out of account. So every section for given value of x, is again, except for the modifications inside the said limits of temperature, the well-known figure in which the lower branch passes continuously into the upper branch. Let us now think the line p_{123} as function of T traced in every section. Only for so far this line lies between the upper and the lower branch of the section of the modified surface of saturation, the mixture of the chosen value of x can split up into three phases. If this line intersects either the upper branch, or the lower branch, and if therefore part of the line p_{123} lies outside the surface of saturation, this must be considered as a parasitic branch, at least for the mixture chosen. So the dotted lines of fig. 39 and fig. 40 represent the values of T for which the line p_{123} intersects a chosen section of the surface of saturation. And so the question whether in fig. 40 the situation of point Q'_1 is such that another point occurs in the dotted curve for this value of x, coincides with the question whether there exist sections for which the line p_{123} intersects the saturation curve twice. As $\frac{V_{21}}{x_2-x_1}$ and $\frac{V_{31}}{x_3-x_1}$ are negative on the vapour branch according to the formula for the calculation of $\frac{dx_1}{dT}$ a negative value of this quantity is attended with a positive value of $\frac{dp}{dT_{123}} - \left(\frac{dp}{Td}\right)_x$ or with the line p_{123} entering the heterogeneous region with increasing T. Reversely a positive value of $\frac{dx}{dT}$ shows that the line p_{123} enters the homogeneous region with increasing temperature, and therefore appears further only as parisitic branch. Now in the point Q'_2 the value of $\left(\frac{dp}{dT}\right)_{123}$ is equal to the value of $\left(\frac{dp}{dT}\right)_x$, as it is on the section of the surface of saturation for the x of the point Q_1, as follows if in the formula for $\frac{dp}{dT_{123}}$ we put $x_2 + dx_2$ for x_3, V_2+dV_2 for V_3, and $\eta_2 + d\eta_2$

for η_3. Then we find namely

$$\frac{dp}{dT_{123}}=\frac{\eta_1-\eta_2-(x_1-x_2)\dfrac{d\eta_2}{dx_2}}{v_1-v_2-(x_1-x_2)\dfrac{dv_2}{dx_2}}.$$

For $\frac{d\eta_2}{dx_2}$ and $\frac{dv_2}{dx_2}$ we may write $\left(\frac{d\eta_2}{dx_2}\right)_{pT}$ and $\left(\frac{dv_2}{dx_2}\right)_{pT}$ because the phases 2 and 3 then have equal p and T. Now the point Q_1 is a liquid phase, and so a point of the upper sheet of the surface of saturation. In general the value of $\left(\frac{\partial p}{\partial T}\right)_x$ for such a point is not great at low temperatures. But yet it is larger on the whole than the value of $\left(\frac{\partial p}{\partial T}\right)_x$ on the vapour sheet, even for sections for which x is smaller. At least for temperatures which lie pretty far from T_k, so that there are therefore two possibilities chiefly dependent on the temperature: either the value of $\left(\frac{\partial p}{\partial T}\right)_x$ in the point Q_1 may be larger than $\left(\frac{\partial p}{\partial T}\right)_x$ for the point Q'_1, or smaller — and so the value of x for the point Q'_1 may either run back or proceed.

Over the full width of the three-phase-curve on the right of Q_2 the line p_{123} leaves the upper sheet of the surface of saturation with rising temperature. This is also still the case for points on the left of Q_2; but a point will soon occur where the three-phase-curve passes to the lower sheet. So this point must lie on the "contour apparent" with regard to the T, x-surface; or in other words: it must be a critical point of contact. Then too the three-phase-curve still passes to smaller value of x. And only afterwards a point can occur where x has minimum value, but this only on the lower sheet. And if the temperature of Q is comparatively low, the vapour branch of the three-phase-curve will certainly run again to the right with falling temperature. Accordingly I have drawn the vapour branch in fig. 39 in this way, though there too the circumstance may occur that x runs back. Besides, the circumstance occurs there that x shows minimum and maximum value for the liquid phases. The condition for x, whether maximum or minimum is $\left(\frac{\partial p}{\partial T}\right)_{x_{\rm II}}=\left(\frac{\partial p}{\partial T}\right)_{x_{\rm III}}=\frac{dp}{dT_{123}}$, if we denote the phase where x runs back, by 1.

But let us return after the discussion of these particularities, to the treatment of the T, x-projection of the closed curve.

We have already observed that the point P is not found when the surfaces $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}=0$ do not intersect. Reversely P extends to a curve if the surfaces do not only touch, but intersect. We obtain the equation of this closed curve, if we solve the value of $\frac{v}{b}$ from the equation:

$$\frac{v}{b}(1-A)-2\frac{v}{b}+(1+B)=0$$

and substitute it in $\frac{d^2\psi}{dx^2}=0$ or $\frac{d^2\psi}{dv^2}=0$. It is simplest to do this in $\frac{d^2\psi}{dv^2}=0$, or $MRT=2\frac{a}{b}\frac{\left(\frac{v-b}{b}\right)^2}{\left(\frac{v}{b}\right)^3}$; or to substitute the value of $\frac{b}{v}$ in $MRT=2\frac{a}{b}\left(\frac{b}{v}\right)\left(1-\frac{b}{v}\right)^2$. If we write $\frac{b}{v}$ in the following form:

$$\frac{b}{v}=\frac{1\mp\sqrt{A-B+AB}}{1+B}=\frac{1\mp\sqrt{X}}{1+B}$$

and

$$1-\frac{b}{v}=\frac{B\pm\sqrt{A-B+AB}}{1+B}=\frac{B\pm\sqrt{X}}{1+B}$$

we find:

$$MRT=2\frac{a}{b}\frac{(B^2-2BX+X)\pm(2B-B^2+X)\sqrt{X}}{(1+B)^3} \quad . \quad . \quad (1)$$

When $X=A-B+AB=AB\left\{\frac{1}{B}-\frac{1}{A}+1\right\}$ is positive, T is real, and there are two values of T for every value of x. For the same values of x for which in the v, x-projection the two values of $\frac{v}{b}$ coincide, the two values of T coincide in the T, x-projection. The values of T assume a simple form for these limiting values of x, because then $X=0$, i.e. $MRT=2\frac{a}{b}\frac{B^2}{(1+B)^3}$; of course this value must also hold for the case that these limiting values of x coincide, which we treated above. We can even simplify this form of MRT for the calculation and obtain the form:

$$MRT = \frac{2c}{b_1(n-1)^2}\,[1+(n-1)\,x]\,\frac{1}{\left\{\frac{1}{(n-1)^2}\,\frac{1}{x}+\frac{n^2}{(n-1)^2}\,\frac{1}{1-x}\right\}^2}$$

by writing $b\,\frac{\frac{1}{b^2}}{\frac{1}{a}} = b\,\frac{\frac{x\,(1-x)}{b^2}}{\frac{x\,(1-x)}{a}} = \frac{cb}{\left(\frac{db}{dx}\right)^2}\,\frac{B}{A}$ for $\frac{v}{b}$.

If we seek the maximum value of T, we find for the determination of x an equation of the 3rd degree, viz.:

$$(1-x)^3 + x\,(1-x)^2\,\frac{3n-1}{2} - n^2x^2\,\frac{3-n}{2} - n^3x^3 = 0$$

and putting $\frac{nx}{1-x} = k$:

$$1 + k\,\frac{3n-1}{2n} - k^2\,\frac{3-n}{2} - k^3 = 0.$$

For $n=1$ we should have $k=1$, for $n=2$ $k=1{,}22$; but for very high value of n $\frac{k}{n}$ approaches to $\frac{1}{2}$. This implies that for $n=1$ the maximum value of MRT lies at $x=\frac{1}{2}$, and for $n=\infty$ at $x=\frac{1}{3}$. For all other values of n x lies between $\frac{1}{2}$ and $\frac{1}{3}$. By the aid of this value of x we can then calculate the highest value of MRT for the points where $X=0$. But the conclusion is not different from that at which we arrived above: viz. that only with n appreciably larger than 3 the value of the temperature can rise to T_k or even to T_{k_1}.

The value which we found in general in equation (1) for the temperature of the points of the closed curve is too intricate to be fully discussed. We can, however, foresee what in general the shape of the T,x-projection will be. For a curve of small dimension the point P of fig. 39 and fig. 40 is to be replaced by a smaller chosed curve which extends according as the former curve itself assumes greater dimensions. Of course the other lines experience the influence of this. Thus in fig. 39 the point P_{ab} will descend and P_{cd} ascend. For every value of x, so of a, b, B and X, the first part of MRT in equation (1), viz.: $2\,\frac{a}{b}\,\frac{B^2+X\,(1-2B)}{(1+B)^2}$ indicates the value of the arithmetical mean, so half the sum of the lowest and the highest temperature; and the second part, viz. $2\frac{a}{b}(2B-B^2+X)\sqrt{X}$ denotes the amount that the really occurring temperatures lie above or below this middle value. This second part is imaginary outside the limiting values of x. For between these limiting values of x, X is positive, and beyond them negative — but the first part exists over the full width. The course of this first may be given in the main points. Beginning with $T=0$ and $x=0$ it ends also with this value at $x=1$. But for very small value of x or $1-x$, provided it be outside the limiting values of x, this first part is negative.

For the limiting values of x, where $X=0$, it has the above treated positive value $MRT=2\frac{a}{b}\frac{B^2}{1+B)^2}$. But just beyond these limiting values of x a value equal to 0 must occur; we conclude to this by noticing that if x or $1-x$ is very small, B^2 and XB may be neglected by the side of B, while X is negative beyond the limiting value of x. The curve which represents the first part begins with an ordinate equal to zero, then descends below the axis, but intersects the axis again before the smallest value of x is reached for which X is equal to zero, then rises to a maximum value, after which it descends below the axis, and finally terminates with a value zero.

So if we draw the curve T_k as in fig. 39, this curve is of course the limit above which T cannot rise for any point of the closed curve. The closed curve being the section of two surfaces which have each a "contour apparent" on the T,x-plane, the projection of the sections cannot fall outside this outline. So the T,x-projection can have either one or two points in common with the curve T_k, in which points it must touch this curve. In these points of contact $\frac{v}{b}=3$. If there are two points of contact $\frac{v}{b}$ is >3 between these points. The observation that $\frac{v}{b}=3$ in the points of contact enables us to show that this circumstance cannot occur for low value of n. First of all not for $n<2$, because, as we saw before, v must there be smaller than $b_2=2b_1$. If we introduce into the equation:

$$\left(\frac{v}{b}\right)^2(1-A)-2\frac{v}{b}+(1+B)=0$$

the condition $\frac{v}{b}=3$, we get:

$$4=9A-B.$$

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Now

$$B = \frac{1}{\frac{1}{(n-1)^2}\frac{1}{x} + \frac{n^1}{(n-1)^2}\frac{1}{1-x} - 1},$$

and A

$$= \frac{1}{\frac{1+\varepsilon_1}{(n-1)^2}\frac{1}{x} + \frac{n^2(1+\varepsilon_2)}{(n-1)^2}\frac{1}{1-x} - 1}.$$

Let us take two extreme cases: 1. the case that ε_1 and $\varepsilon_2 = 0$; 2. the case that $\frac{\varepsilon_1}{(n-1)^2}\frac{1}{x} + \frac{n^2\varepsilon_2}{(n-1)^2}\frac{1}{1-x} = 1$.

In the first case $B = A$, and so $B = \frac{1}{2}$, or it must be possible to find real values for x from the equation: $\frac{1}{(n-1)^2}\frac{1}{x} + \frac{n^2}{(n-1)^2}\frac{1}{1-x} = 3$, which values must, moreover, lie between the limiting values of x, in this case $x = 0$ and $x = 1$. For the roots to be real

$$1 \text{ must be} > \frac{\sqrt{\frac{1}{3}}}{n-1} + \frac{n\sqrt{\frac{1}{3}}}{n-1}$$

or

$$\frac{n+1}{n-1} < \sqrt{3}$$

or

$$n > \frac{\sqrt{3}+1}{\sqrt{3}-1};$$

if the sign $>$ is changed into $=$, there is only one root at $n = \frac{\sqrt{\frac{1}{3}}}{n-1}$ and $1-x = \frac{n}{n-1}\sqrt{\frac{1}{3}}$. So for n about 3.75 $\frac{v}{b}$ will be $= 3$ for $x = \frac{1}{4.75}$, if $\varepsilon_1 = \varepsilon_2 = 0$. Then the closed curve touches the curve T_k in the T,x-projection. But then the lower branch of the T,x-line will have descended to $T = 0$. Then we have to expect fig. 40, however with this modification that P_{ab} lies at a height $= 0$ and the three-phase-pressure is already found at all low temperatures.

In the second case, in which the supposition $\frac{\varepsilon_1}{(n-1)^2}\frac{1}{x} + \frac{n^2\varepsilon_2}{(n-1)^2}\frac{1}{1-x} = 1$ however, involves the assumption that the point for which $\frac{v}{b} = 3$, lies at a value of x which is just one of the limiting values of x, $\frac{B}{1+B}=A$ and the equation $4=9A-B$ yields the value 2 for B. So $\frac{1}{(n-1)^2}\frac{1}{x}+\frac{n^2}{(n-1)^2}\frac{1}{1-x}=\frac{3}{2}$ must then yield real values for x, and so $\sqrt{\frac{3}{2}}$ must be $>\frac{n+1}{n-1}$, or $n>10$.

Now, however, if we assign values to ε_1 and ε_2 the condition of the second case will in general not be fulfilled, and $\frac{\varepsilon_1}{(n-1)^2}\frac{1}{n}+\frac{n^2\varepsilon_2}{(n-1)^2}\frac{1}{1-x}$ will not have risen to 1 — but we shall have to put $\frac{\varepsilon_1}{(n-1)^2}\frac{1}{n}+\frac{n^2\varepsilon_2}{(n-1)^2}\frac{1}{1-x}<1$, or equal to $1-\alpha$, in which α will have a value between 1 (that of the first case), and 0 (that of the second case). And the result will then be that the condition $\frac{v}{b}=3$ will require a value of n which is greater than 3.75, but which need not rise to 10.

But I shall not continue the calculations required for this. If we review what precedes, it appears sufficiently: 1 that the case that three-phase-pressure exists between temperatures that differ little, may occur for all values of n — but that if n is small, these two temperatures lie too low to be observed. It is not possible to give the exact value of n for which these temperatures if they exist, can be observed, before the ratio is known between the temperature at which the two surfaces $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}=0$ touch, and the temperature at which the double plaitpoint has appeared or disappears. 2. That for the case of fig. 40 the required value of n may be estimated as at least 4. 3. That as ε_1 and ε_2 descend below the parabola OPQ, the two temperatures between which three-phase-pressure can exist, diverge further, and that only if ε_1 and ε_2 (we only deal with positive ε_1 and ε_2 here) have become equal to 0, the lowest temperature has descended to the absolute zero point.

If we further take into consideration that the point ε_1, ε_2 lies on the curve $a^2_{12}=l^2 a_1 a_2$, which represents in ε_1 and ε_2 an ellipse, a parabola or a hyperbola according as $l^2<1$ or >1, and that of this curve only those points which lie in the triangle OPQ (below the parabola) yield a closed curve which we have treated, we see that the phenomena discussed do not only depend on n, but that besides special relations must exist for a_1 and a_2 and a_{12}, which are represented by ε_1 and ε_2 positive in the equations $\frac{a_1}{c}=\frac{1+\varepsilon_1}{(n-1)^2}$ and $\frac{a_2}{c}=\frac{n^2(1+\varepsilon_2)}{(n+1)^2}$ and $n-1>\sqrt{\varepsilon_1}+n\sqrt{\varepsilon_2}$. By far the greater part of the curve $a^2_{12}=l^2a_1a_2$ lies outside this region, and the occurrence of the discussed phenomena will, therefore, have to be considered as comparatively rare. If we descend in the region OPQ, so that either ε_1 or ε_2 or both become negative, then (but the consequence of a negative value of ε_1 and ε_2 has not yet been discussed) three-phase-pressure is to be expected already at $T=0$. If we go upwards along the curve $a^2_{12}=l^2a_1a_2$, and if we get above the parabola with ε_1 and ε_2, there is perfect miscibility. (For the values of ε_1 and ε_2 required for perfect miscibility consult Contribution XI p. 443). As the upward movement along the curve $a^2_{12}=l^2a_1a_2$ is attended with decrease of $\frac{pk_2}{pk_1}$, it follows from this that if in analogous cases the ratio $\frac{pk_2}{pk_1}$ decreases, we pass from non-miscibility to perfect miscibility.

The conclusions in the derivation of which we have supposed to treat only normal cases, viz. such for which no chemical action takes place between the two components, or for which each of the components behaves normally, are quite corroberated by the observations. I know only of one exception, namely that the case of fig. 40 occurs also in the observations of KUENEN for mixtures of ethane and aethylalcohol, etc. In this case we have to put n either below or just above 2. How it is that the abnormal behaviour of alcohol has here an influence as if n were increased, cannot be accounted for as yet. But in the cases of BÜCHNER for mixtures of carbonic acid and organic liquids, for which also fig. 40 gives the course schematically, n will, no doubt, have the value found by calculation. (BÜCHNER, Thesis for the doctorate 1905).

In conclusion a few remarks.

1. In fig. 30 of Contribution VI I have already given the course of the plaitpoint line for the case of fig. 39, and also of the three-phase-pressure of T.

2. The upper and the lower sheet of the surface of saturation are subjected to some modification in the case of fig. 39 only between the two temperatures between which there is three-phase-pressure. The modification for the upper sheet consists in what follows. Between the limiting values of x of the dotted closed curve of fig. 39 the

upper sheet is raised. At the limiting values of x this rise is still equal to zero.

But for values of x, which differ from these limiting values, the rise assumes certain values, at first, however, only between temperatures which differ little. But this is accurately rendered by fig. 39. The consequence of all this is that if a certain increase of pressure is applied, e. g. if we observe above the maximum pressure of the modified liquid sheet, the total non-miscibility has disappeared. If we lower the pressure, the non-miscibility may reappear but at a pressure which is only slightly less than the maximum pressure it exists only over a very small range of temperature. In other words there the dotted curve of fig. 39 has greatly contracted. In this two cases will no doubt occur, either real minimum pressure occurs, or the pressure in the point Q is the highest. At higher temperatures, however, splitting up into vapour and liquid is still possible.

3. If in fig. 40 the circumstance occurs of minimum value of x on the vapour branch, there exists for some mixtures, if we take care to follow the three-phase-pressure, retrogression of the condensation.

For the mixtures which show the above discussed non-miscibility between two temperatures, both a^2_{12} may be $> a_1\, a_2$, and a^2_{12} may be $< a_1\, a_2$. However if $a^2_{12} > a_1\, a_2$, the chance to non-miscibility is smaller. In this case the points ε_1, ε_2 lie on a hyperbola which intersects the space OPQ below the parabola close to the point Q; and as the intersection takes place nearer to Q, the distance between the parabola and the ε_2-axis is smaller. And as soon as the value of $\frac{a_{12}^2}{a_1 a_2}$ would become so large that the intersection of the hyperbola with the ε_2-axis takes place past Q, non-miscibility will be quite excluded. So if $\frac{a_{12}^2}{a_1 a_2} > \frac{1}{4}\frac{(n^2+1)^2}{n^2+(n-1)^2}$. For the full discussion of the intersection of the surfaces $\frac{d^2\psi}{dx^2}=0$ and $\frac{d^2\psi}{dv^2}=0$ it now remains to examine the cases with negative values of ε_1 and ε_2.

(March 25, 1909).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday March 27, 1909.

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Physiology — *"The permeability of blood-corpuscles to calcium."* By Prof. H. J. Hamburger.

(Communicated in the meeting of October 31, 1908).

It is beyond doubt at present that red blood corpuscles are permeable to anions. This was first established for chlorine by quantitative chemical determinations [1]), and also with respect to other anions no reasonable doubts exist as to their power of permeating the blood corpuscles [2]). This is not the case with metal ions or kations. It is generally believed that blood corpuscles are absolutely impenetrable to these. This opinion seems to be founded on an experiment by Gürber [3]). This investigator led carbonic acid through a suspension of red blood corpuscles in a NaCl solution, and found that chlorine penetrated into the blood corpuscles, but that the amount of potassium and sodium in blood corpuscles and liquid remained the same. The blood corpuscles thus would seem to be impenetrable to both these kations, and this supposition has the sooner found belief as in normal conditions the potassium is found chiefly in the blood corpuscles, the sodium in the serum. Tacitly the impenetrability of erythrocytes to Na and K seems to have been extended to the other kations and various authors have even quite recently expressed themselves to this effect [4]).

Investigations, however, carried on jointly with Hekma, concerning the influence of various substances, and especially of small quantities of Ca on phagocytosis have shaken my belief in the truth of this view. The fact that phagocytosis and, as I afterwards discovered, chemotaxis as well are greatly increased by traces of Ca suggests the question whether Ca does not enter into the white blood corpuscles.[5])

The strict proof of this could only be given by quantitative chemical determinations. But the difficulty is that white blood corpuscles are hard to obtain in great quantities. This does not apply to red blood corpuscles, and as these have never shown themselves different as to permeability from the white ones it seemed advisable to make our investigations on the former.

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[1]) Hamburger. De permeabiliteit der roode bloedlichaampjes in verband met de isotonische coefficiënten. Proceedings of the Royal Academy of Science. Series III, Vol VII, 1889. — Over den invloed der ademhaling op de permeabiliteit der bloedlichaampjes. Ibid. Vol. IX, 1891. — Zeitschr. f. Biologie **26** 1889 S. 414; 1892 S. 405.

[2]) Hamburger. Report of the meeting of the Royal Academy of Science. Oct. 27. 1900. Hamburger und van Lier. Archiv f. (Anat. u.) Physiol. 1902 S 492.

[3]) Gürber. Sitzungsber. d. med. physik. Gesellsch. zu Würzburg 25 Febr. 1895.

[4]) Cf e. g. Höber in the Handbook of von Korányi and Richter, 1907. p.p. 287 and 288.

[5]) Hamburger and Hekma, Proceedings of the Royal Ac. of Science. June 29, 1907.

Various methods have been chosen for this purpose. In the first place red blood corpuscles after being mixed with an isotonic cane sugar solution were washed with NaCl solutions, and it was then found that Ca had entered into these salt solutions. It might however be objected to these experiments that the red blood corpuscles, after being washed in a sugar solution, are no longer in a physiological condition and on account of that had become permeable to Ca.

Therefore the experiments were repeated in another way viz. by adding slight quantities of substances to the serum occurring in it also under normal conditions. First we added to the blood 0.024°/₀ and 0.012°/₀ $CaCl_2$. Then serum and blood corpuscles were examined as to the amount of Ca they contained, and this was compared with the amount of Ca found in serum and blood corpuscles of the blood used in our first experiment. If no Ca entered into the blood corpuscles, all the Ca added would be found in the serum. If part of the Ca passed into the blood corpuscles, this would be discovered as well, and as a test it might be investigated to what extent the joint increase of Ca in blood corpuscles and serum corresponded with the Ca added.

We subjoin a table which will need no further explanation. This table also contains the result of an experiment answering the question whether erythrocytes, having absorbed Ca from a serum containing Ca, lose their Ca again when brought back into their normal serum, in other words whether blood corpuscles also are *extrameable* to Ca.

In explanation to this table must be added that the Ca determinations have been made by burning the dried masses and extracting the ashes with dil. HCl and adding alcohol and H_2SO_4 to the clear filtrate, Ca being thus precipitated as $CaSO_4$. Finally we must add that in these experiments 80 ccm. of cow's blood were used consisting of 32.4 ccm. blood corpuscles and 47.6 ccm. serum.

(1). 32.4 cc. *blood corpuscles* of blood *mixed with* 0.024°/₀ *$CaCl_2$* supply after being washed with a canesugar solution **0.0458** gr. $CaSO_4$.

(2). 32.4 cc. *blood corpuscles* of blood *mixed with* 0.024°/₀ *$CaCl_2$* supply after being washed with serum and afterwards with a canesugar solution . . . . **0.0361** gr. $CaSO_4$.

3). 32.4 cc. *blood corpuscles of normal* blood supply after being washed in a canesugar solution . . . **0.0354** gr. $CaSO_4$.

(4). 32.4 cc. *blood corpuscles* of blood *mixed with* 0.012°/₀ *$CaCl_2$* supply after being washed in a canesugar solution **0.0398** $CaSO_4$.

(5). 47.6 cc. *Serum* of the blood *mixed with* $0.024^{0}/_{0}$ $CaCl_2$ supplied . . . . **0.0492** gr. $CaSO_4$

(6). 47.6 cc. *Serum* of the blood *mixed with* $0.024^{0}/_{0}$ $CaCl_2$ supplied . . . . **0.0492** gr. $CaSO_4$.

(7). 47.6 cc. of the normal original serum supplied **0.0369** gr. $CaSO_4$.

(8). 47.6 cc. *Serum* of the blood *mixed with* $0.012^{0}/_{0}$ $CaCl_2$ supplied . . . . **0.0437** gr. $CaSO_4$.

(9). 47.6 cc. Serum to which the same amount of $CaCl_2$ had been added as to the corresponding 80 cc. blood as sub (1) and sub (5) and (6) supply . . . . . . **0.0596** gr. $CaSO_4$.

Comparison of the values in this table shows:

1. *that Ca has entered into the blood corpuscles* (Cf. (3) with (1) and (4);
2. *that the blood corpuscles give up this Ca when brought back into* normal serum. (Cf. (3) with (1) and (2).
3. *that the entire amount of Ca added to the blood is found back in blood corpuscles and serum.*

Moreover this table demonstrates that in the blood corpuscles of normal blood Ca is found (Cf. (3)).

This last result clashes with the general opinion that in blood Ca is exclusively found in the serum. In the well known tables of **Abderhalden** on the quantitative analyses of various kinds of blood, for instance, we find that everywhere Ca is being stated as absent from the blood corpuscles, and in **Fränkel**: "Descriptive Biochemie" p. 557 we read: "Das Calcium ist lediglich im Serum enthalten."

What may be the cause of this contradiction? We think that it is to be found in the method used for the quantitative determination of Ca. We know the metal has been determined as a sulphate or an oxalate, and it was tacitly taken for granted that these compounds are quite insoluble in the fluids in which they are found or very nearly so. This is by no means the case, especially not when the volume of the fluid is considerable. Close determinations of the solubility of $CaSO_4$ in acid alcohol have shown me that, besides a slight precipitate always visible after 24 hours, a great part of the $CaSO_4$ remains in solution.

When we take this solubility into consideration it is found that the blood corpuscles contain a by no means negligible quantity of Ca, as is plainly shown by the figures in the preceding table.

Still another method was applied to investigate the permeability to Ca.

If the view expressed by J. LOEB and others is a correct one, viz. that when a NaCl solution is added to cells an interchange takes place between Na-ions of NaCl and other kations of the cells, it may be expected that an addition of NaCl to the bloodserum will bring about a transition of Ca-ions from the blood cells to the serum. To investigate this, 0.1°/₀ and 0.16°/₀ NaCl were added to the blood serum of a known amount of blood, increases also occurring in normal and a fortiori in pathological life and leaving intact the life of phagocytes (HAMBURGER and HEKMA, l. c.). Next the amount of Ca in the serum was determined and compared with that of the original blood. The Ca amount was determined by adding ammonium oxalate and measuring the volume of the Ca oxalate in funnelshaped capillary tubes.

The result of these Ca-determinations however by no means answered our expectations. Instead of increasing a decrease was found, as shown by the last column of the following table.

Na Cl added to the serum.	Dilution of serum.	Decrease of Ca amount of serum.
0.1 %	9.6 %	21.8 %
0.16 %	12 2 %	29.5 %

To what could this decrease be attributed?

To the dilution of the serum perhaps, which being made hyperisotonic, had extracted water from the blood corpuscles? In the second column the percentage of the dilution is stated. If this were entirely responsible for the decrease in percentage of the Ca amount, the values in the two columns would entirely agree. We see that this is not the case and that the Ca amount in the serum has decreased more than is consistent with the dilution. We must infer from this that under the influence of NaCl, Ca has passed into the blood corpuscles.

It seemed to me that this could only be explained by assuming that in consequence of the loss of water a modification in the dissociation had taken place in the blood-corpuscles and that this modification was to be held accountable for the fact. If this were the case the addition of an isosmotic quantity of a non-electrolyte to the serum, of canesugar for instance, would equally result in a transition of Ca to the bloodcorpuscles, and that the decrease of Ca would be even greater than where NaCl was added.

Thus the following mixtures were made:

1	100	serum	+ 0.1	gr.	NaCl.
2	100	„	„ 0.2	„	„
3	100	„	„ 0.3	„	„
4	100	„	„ 0.884	„	canesugar
5	100	„	„ 1.76	„	„
6	100	„	„ 2.55	„	„

Of these 6 solutions and for the sake of comparison also of normal serum, 20 cc. were added to 20 cc. of the same bloodcorpuscles. After being mixed, the suspensions were left to themselves for an hour, after which the amount of Ca in the serum was determined. A summary of the results is found in the following table:

	Volume of Ca-oxalate	Decrease of Ca in serum in %
Unmixed serum.	39	
1. serum + 0.1 % Na Cl	33	15.3%
2. „ „ 0.2 „ „ „	29	25.6%
3. „ „ 0.3 „ „ „	25	36. %
4. „ „ 0.884 „ canesugar	30	23 %
5. „ „ 1.76 „ „	28	28.3%
6. „ „ 2.55 „ „	22	43.6%

Examination of this table will show plainly that indeed the addition of canesugar has caused a considerable transition of Ca from the bloodcorpuscles to the serum, and further that in accordance with our supposition the isosmotic NaCl solutions caused a somewhat slighter transition.

The principal cause for the transition of Ca into the blood corpuscles by the addition of some substance to the serum must be sought in the fact that the blood corpuscles lose water on account of this addition; in other words: *an increased osmotic pressure of the serum causes a transition of Ca to the blood corpuscles.*

If the increased osmotic pressure is caused by a salt (electrolyte) a movement of the calcium in the opposite direction takes place under the influence of the kation of the salt; but this movement is much less important.

In this connection it must be pointed out that the phagocytary power is considerably impaired already by a slight increase of osmotic pressure of the medium, and that the nature of the substance occasioning the increase of osmotic pressure is not without importance indeed, but plays a subordinate part.[1])

More explicit communications on the investigations discussed in this paper will appear elsewhere.

Physiology. — "*About Observations on the electro-myogram and form-myogram under the influence of fatigue.*" By Dr. A. K. M. Noyons, assistant in the Physiological Laboratory at Utrecht. (Communicated by Prof. H. Zwaardemaker.)

(Communicated in the meeting of December 24, 1908).

As a consequence of my investigations in which the independence of the electro-cardiogram with regard to the form-cardiogram [2]) came to light, the question rose whether also for a skeleton-muscle a similar independence exists between electric changes and changes of form under certain definite circumstances. In order to get data with respect to this I started from the principle that in the course of a process of fatigue, arisen by regularly repeated stimulation, different forms of contraction with changes in crescente and different forms of contraction-state as tetanus and tonus can be revealed.

It is the mutually deviating physiological conditions in the course of a process of fatigue which, as might be expected, with the existing independence of mechanical and electric reaction upon the same stimulus, would sooner or later break the congruence of these reactions prevailing at a given moment. Not long ago Brücke [3]), testing the data of Martius, Waller, Garten and Durig pointed out cases of troubled parallelism. These investigators, in order to make the action-current visible, have made use of the capillar-electrometer, whereas I regularly availed myself in my investigations of the string-galvanometer of Einthoven (Edelmann's small model).

In order to cause contraction of the muscle both mechanical and electric stimuli have to be considered. The stimulation takes place indirectly with the M. gastrocnemius of Rana. The electric and form-changes are registered by means of photography. The muscle is with the knee fastened to a substratum; the M. gastrocnemius is prepared free from the other muscles, whilst the Achilles-tendon by means of a thread is connected with a small lever bearing a counterpoise which is moved up and down at every muscular motion along a pulley. The muscle acts at a distance of 2,6 cm. and the weight to be lifted at a distance of 5 cm. from the fulcrum of the lever. The long lever-arm moves past the slit of the registration-box and thus throws a shadow on the sensitive paper of the registration-box, while at the same time the string-movements and the time-writer are photographically registered. The M. gastrocnemius is carefully kept free from the other muscles to avoid the influence of the contractions and electric phenomena of the other unencumbered muscles. The M. gastrocnemius is led to the string-galvanometer by means of the unpolarizable magazine-electrodes with moveable cotton-seeds. One electrode usually finds itself on the thickest part of the muscle, while the other is placed more proximally. In the last series of experiments the electrodes-seeds with an alteration in SAMOIJLOFF's manner, were, by means of a thin thread, drawn through the muscle-fascia, fixed to the surface of the muscle, in order to be sure that always the same points were led to the string-galvanometer.

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[1]) Hamburger en Hekma. These Proceedings June 1907.

[2]) Noyons., A. K. M. About the Independence of the electro-cardiogram with regard to the form-cardiogram. These Proceedings October 31, 1908.

[3]) Brücke., E. Th. v. Ueber die Beziehungen zwischen Aktionstrom und Zuckung des Muskels im Verlaufe der Ermüdung. Archiv f. d. ges. Physiologie Bd. 124, 1908.

§ 1. *Mechanical stimuli.*

The mechanical stimuli have been obtained in one series of experiments by falling drops of mercury from the mercury dripping apparatus of SCHÄFER[1]), whilst in another series of experiments the tapping hammer of the tetanomotor of HEIDENHAIN produces the mechanical stimulus.

a. *Experiments with falling drop of mercury.*

SCHÄFER's apparatus is placed in such a way that at first, the drops are let fall on a sheet of glass, inserted between nerve and opening of the drip-tube. At a given moment when a somewhat regular dripping has been obtained, the sheet of glass is drawn away and the nerve itself is hit by the drops, whilst then the registration takes place.

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[1]) SCHÄFER, E. A. A. Simple apparatus for the mechanical stimulation. Proceedings of the physiol. Society. Jan. 1901.

Along a somewhat sloping substratum, on which the nerve rests in a groove, the drops of mercury rapidly flow away. By changing the frequency of the drops and altering the height of their falling, often also spontaneously without any alteration in the external conditions for the experiment, all kinds of discongruencies may be seen to show themselves between the mechanical and electric reactions of the muscle. Beautifully regular curves of fatigue, are in this way difficult to obtain, as it is not always possible to bring about an always equal fall of the drops of mercury, as to frequency and direction. The curve in fig. 1, got in the above way, proves that the electric phenomenon of the succeeding contractions in the case in question every time has the same course and the same amplitude. In contradistinction to this the mechanical effect is repeatedly unequal.

b. *Experiments with the tapping hammer.*

The tetanomotor of Heidenhain is thus linked in a chain with a chronoscope as interrupter that only twice a second the hammer hits the nerve in the isolated ivory groove. To preserve the nerve as much as possible from too rapid lesion, a bit of muscle tissue, to break the thrust of the hammer, is laid across under the nerve. The nerve itself is, by means of a little windlass, slightly strained. On the whole it is very difficult to regulate the fall of the tapping hammer and the tension of the nerve so as to make the stimuli every time follow by a regular series of mechanical and electric reactions. Now and then, however, it is possible to make a good series, as fig. 2 subjoined shows.

It is seen how the series in fig. 2 begins with a large, initial, mechanical and electric reaction, followed by the others which are directly much smaller. At the same time there takes place after the first reaction a removal of the zero-position, first in one direction and then in the opposite direction. On the whole the form- and electromyograms are well nigh congruent. Now and again we see how the muscle with a compound contraction reacts upon a single stroke of the hammer.

To dose exactly and administer a better, always the same, local stimulus, the electric stimulus was in the course of the further investigations made use of.

§ 2. *Electrical stimuli.*

As electric stimuli were used the opening- and closing-currents either of a faradaic or of a galvanic current, which was interrupted either by means of an interrupter fixed to KAGENAAR's chronoscope of $^1/_2$ second with swinging platina-contacts, or by means of the rheotome-apparatus of ENGELMANN connected with a kymographion. With this rheotome-apparatus the stimuli were on the whole less frequent and the contactstoppers were placed so as to make the closing- and opening-stroke follow each other with well nigh equal intervals of 2 seconds. The following objections, however, can be raised to these methods of stimulation. In the course of the process of fatigue the muscle sooner or later, owing to the weight to be raised, the size of the stimulus, its frequency and the previous history of the muscle itself, comes into such a condition that the muscle is perhaps still potentially able to execute contractions, but is accidentally prevented from doing so by tetanus respectively tonus. Further we are, especially with the rheotome-apparatus, at which the stimuli as a rule cannot nearly be deemed equivalent, not entitled to make comparisons between the respective mechanical and electrical reactions at different periods of the process of fatigue. Therefore another series of experiments was made, in which the muscle, it is true, in the manner described just now was tired by means of opening- and closing-stimuli of a constant current, but in which during the whole course of this process of fatigue the muscle was at regular intervals examined in its mechanical and electric reactions by means of a single closing-induction-stroke. Every time, however, before this closing-induction-stimulus was administered, the muscle was first allowed to become perfectly lax. In making the experiment a POHL-swing without a connecting cross was made use of, by which the nerve could be stimulated at will, either by the periodical interruptions of the constant current, or by the single closing-stroke, obtained by the falling-apparatus of BERNSTEIN, in the primary chain of an inductorium. The usual provisions were made, see GARTEN [1]), to prove that the electric phenomena do not originate in artificial current-loops.

As a demonstration I give here a short review of one of the experiments from the last series.

Brains and spinal marrow of a Rana fusca have been destroyed.

The M. gastrocnemius, arranged for the experiment in the above manner, is stimulated indirectly, alternately with a breaking galvanic current of 2 volts, or with a faradaic current of 2 volts at a distance of secondary bobbin on 57. The weight to be raised amounts to 75 grammes.

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[1]) GARTEN S. Elektrophysiologie. Handbuch der Physiologische Methodik p. 470.

The string-galvanometer with permanent magnet is used at moderate strain of the string (15 from 60 degrees).

The experiment is begun by stimulating the muscle with a single closing-inductionstroke, after which the periodical galvanic stimulating follows.

In the beginning of this galvanic stimulating the muscle answers with separate contractions, but is soon in tetanus. After some time the muscle is again stimulated by the closing-inductionstroke. The mechanical and electrical effect hereof has increased. The photographic registration shows how the electric phenomena as an answer to the stimulus by means of the interruptions of the galvanic current in general have increased, also how the reaction on the single inductionstroke begins to decrease again in size. The tetanus is attended with a total removal of the rest-position of the string.

In fig. 3 it is seen, how the muscle under the influence of the fatigue now shows a slight electric phenomenon as a reaction upon the periodical opening and breaking of the constant current, besides how the electric phenomenon as an answer to the closing induction-stroke is pretty considerable, but is not accompanied by a mechanical reaction which is not even to be observed as tetanus at the galvanic stimulus. The muscle namely has entirely become slack. The electric phenomenon of the induction-stimulus has become complicated and stretched.

$1^3/_4$ hours after the commencement of the experiment the muscle shows neither mechanical nor electric reaction either on galvanic and on faradaic stimulus. Only when the faradaic stimulus is strengthened the electric reactions become visible again.

Summa summarum, the following, with respect to our subject, most important facts may be gathered from the series of experiments mentioned before and partly described there. In the first place it appears that under definite circumstances, in this case fatigue, also for a skeleton-muscle like the M. gastrocnemius, an independence comes to the front of electric and form-changes of the muscle. It further appears that the more or less congruency of the above reactions is dependent on different factors, among others the strength of the animal.

In general I got, even with the slack M. gastrocnemius of Rana, the same results, as to change of length and mechanical reaction, as Brücke found for the M. sartorius, as to change of thickness and

electric reaction expressing himself as follows: "Während der Ermüdung nehmen Zuckung und Aktionstrom ab, und zwar ging die Abnahme der Aktionströme bei wenig kräftigen Muskeln der der Zuckungen annähernd parallel, wenn man die Zuckungshöhe und die electromotorische Kraft der Aktionströme dem Vergleiche zu Grunde legt. Bei besonders kräftigen Tieren war dagegen deutlich zu erkennen, dass diese Parallelität keine strenge Gesetzmässigkeit darstellt, denn in diesen Fällen hielten sich die Aktionströme auch dann noch auf ihrer ursprünglichen Stärke, wenn an den Zuckungen schon deutliche Ermüdungszeichen zu erkennen waren".

The grade-formations of the electric and mechanical phenomenon are not identical. It further appears that the effect of an induction stimulus working now and then upon the slack muscle is changeable. In the beginning of the process of fatigue namely the effect increases, to decrease later on again. This decrease in size is attended by a stretching both of crescent and decrescent. The electric phenomenon now and then yields a complicated image. Fig. 3. Already Durig [1]) knew such a complicated reaction on a single stimulus; also Garten, Hofmann, Brücke [2]), and Samoijloff [3]) have observed this in a normal muscle.

It appears that in the course of a process of fatigue the proportion of KS > AO as to the electric reaction ofter undergoes a change, and that in such a way, that as a rule the difference between KS and AO gradually becomes smaller so that KS and AO are equal, which generally does not happen before every separate mechanical reaction of the muscle has entirely left off. It sometimes happens that the KS under the influence of the fatigue is in the end < AO. If we make experiments with rather weak currents, it may happen that in this way, both the electric and mechanical reaction on the opening-stimulus do not show themselves for some time, to appear again towards the end of the process of fatigue only with an electrical reaction. Some of the above mentioned facts have in passing been indicated by Samoijloff. These facts might be considered as the manifestation of an "Entartungsreaction". In the same way the slackened crescent and decrescent (of the mechanical as well as of the electric reaction) may be looked upon.

Further we often see that in the course of the process of fatigue

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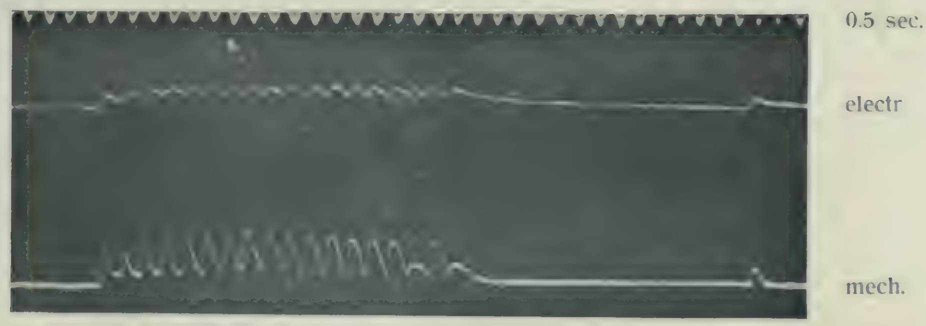
[1]) Durig A. Ueber die elektromotorischen Wirkungen des wasserarmen Muskels, Pflüger's Archiv, Bd. 97, 1903.

[2]) Brücke E. Th. v. l. c.

[3]) Samoijloff A., Einige Elektrophysiologische Versuche. Le Physiologiste Russe 1908. Vol. V, N⁰. 86—90.

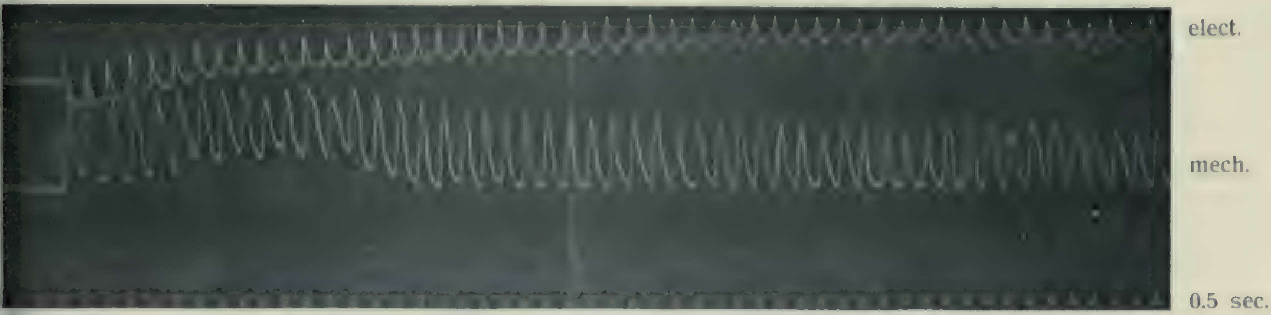
A. K. M. NOYONS. "About Observations at the electromyogram and form-myogram under the influence of fatigue."

Fig. 1.



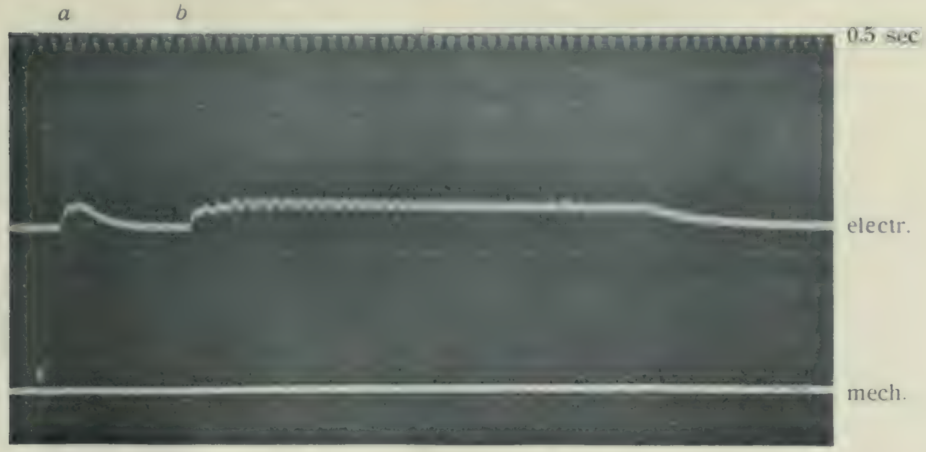
Fatigue-curves of mechanical and electric reactions as answer to stimulation by means of falling drops of mercury. The time is given in $^1/_2$ seconds. The middle line gives the electro-myogram, the third curve the form-myogram.

Fig. 2.



Fatigue-curve of mechanical and electric reactions as answer to the mechanical stimulus of the tetamotor-hammer. The upper line gives the electro-myogram, the next curve the form-myogram and the lowest line the time in $^1/_2$ seconds.

Fig. 3.



Fatigue-curve of mechanical and electrical reactions on the faradaic stimulus (*a*) and on the galvanic stimulus (*b*). The second curve gives the electro-myogram, and the third the form-myogram.

15$^1/_2$ minutes after commencement of the experimenent.

the original diphasic character of the action-current gets lost and is replaced by a monophasic image. We see as it were one top of the electromyogram wear off, whereas the other top increases, as already LEE [1]) observed for the M. sartorius. Also BERNSTEIN and GARTEN [2]) saw this.

The peculiar fluctuations that are often seen at the end of a mechanical fatigue-curve, also show themselves in the electric fatigue-myogram, even in those moments when every mechanical reaction has already disappeared. These fluctuations appear sooner and are much more intense, when the whole animal is narcotized with chloroform or ether. In narcotization the action-currents on the whole remain longer in existence than the mechanical effects. Warming the whole animal with due regards to provisions to prevent even the slightest desiccation, make the mechanical as well as the electric reactions on the periodical stimulus increase strongly in size, notwithstanding the fatigue ought already to manifest its influence on the size of both the phenomena.

Lastly it may still be mentioned here that, after a short fatigue of muscles at weak electric reflex-stimuli and a small weight to be raised, I saw, when stopping the artificial stimulus, spontaneous contractions appear, which continued for some time [3]). What was striking here was that these spontaneous mechanical phenomena were as large as those at electric reflex-stimulation, but that at the same time the accessory electric phenomena were much smaller compared with those obtained by artificial stimulation.

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[1]) LEE F. S. Archiv. für Physiologie 1887.

[2]) BERSTEIN, GARTEN e. a. Handbuch der Physiologie des Menschen von W. NAGEL, 2e Hälfte, Erster Teil, 4e Band, 1907.

[3]) It may be provisionally mentioned here that to complete SAMOYLOFF's work I succeeded. also in a reflectorical way, in obtaining considerable mechanical and electric reactions from the M. gastrocnemius, both in consequence of chemical and mechanical reflex-stimulation.

Chemistry. — "*A contribution to the photo-chemistry of silver* (*sub-*) *haloids*". By Mr. A. P. H. TRIVELLI. (Communicated by Prof. S. HOOGEWERFF).

(Communicated in the meeting of January 30, 1909).

Introduction.

Previous investigations into the photo-chemical decomposition of silver haloids led to the following formula:

$$2\ AgHal \rightarrow Ag_2Hal \rightarrow 2\ Ag.$$

It is true the great variability in the chemical composition of the photo-chemically formed subhaloid has given rise to doubts as to the correctness of the formula Ag_2Hal, so that J. M. EDER [1]) even thinks it possible that the subhaloid has the formula Ag_3Hal_2, Ag_4Hal_3 or perhaps $Ag_{20}Hal_{19}$, but a satisfactory explanation of these deviations was found by GUNTZ [2]) in the partial and only superficial photo-chemical decomposition, so that when quantitative determinations were made, the subhaloid dealt with was never pure, but always contaminated with AgHal and Ag. It is a fact that with continued light action the photo-chemical decomposition of the silver chloride never reaches the formula Ag_2Cl, but approaches it [3]). Thus RICHE [4]) found, after silver chloride had been exposed to the action of light for $1\frac{1}{2}$ years, a composition corresponding to the formula Ag_3Cl_2.

In 1895 O. WIENER [5]) discovered the colour formation of the Seebeck-Poitevin photo-chromics by mechanical colour accommodation, which can only set in, if there are a number of mutually different subhaloids. E. BAUER [6]) took these to be four "modifications" of one and the same subhaloid. A little more than a year afterwards J. M. EDER [7]) in his excellent investigations as to the substance of the latent image came to the conclusion that there exist a number of subhaloids, which consecutively originate photo-chemically one from another, react differently on developers, sodium thiosulphate, ammonia, etc., and are formed anew by oxidation (nitric acid) in the opposite order (as compared with the photo-chemical decompositon). These results, however, require a slight correction, because J. M. EDER started from the idea then still generally held, but now antiquated, that the process of development was nothing but a simple reduction of the unstable subhaloid-bearing silver haloid grain, whereas according to the more recent view, enunciated by W. OSTWALD [8]), K. SCHAUM and W. BRAUN [9]), and confirmed microscopically by

W. SCHEFFER [10]), every development consists in the precipitation of the reduction products from a dissolved silver compound upon the germ-subhaloid. Making use of this, in an investigation into solarization and further properties of the latent image, I [11]) have arrived at the result that the α subhaloid of the latent image passed, with loss of halogen, into another, the β subhaloid. Soon afterwards B. WALTER [12]), without being acquainted with my work, concluded from fresh investigations into solarization, that his experiments are best accounted for if *two* really different "Zerfallstufen" (stages of decomposition) of silver bromide are assumed. Although, consequently, the existence of a number of subhaloids differing in chemical composition and having different properties, has been proved, E. BAUER's modification theory may still be maintained by the side of it, for one of these subhaloids might possess the power of forming a modification by the action of light, through which its absorption spectrum might change, as e. g. white P_4 is transformed by light into orange-coloured P_8. Only if it were proved that this change of colour of the subhaloid was accompanied by a change in the chemical composition of the subhaloid, would the modification theory have to be relinquished. I shall revert to this question later on, and assume for the present that every subhaloid of a definite chemical composition is characterized by its absorption spectrum.

During the last few years LÜPPO-CRAMER [13]), on the ground of a number of chemical reactions and physico-chemical phenomena, has drawn the conclusion that silver subhaloids, with the exception of subfluoride, do not exist, and are nothing but absorption compounds of collodial silver and silver haloid, and he has maintained the direct photo-chemical formation of silver from silver haloid. A short time ago I [14]) succeeded in showing in a paper on silver subhaloids that all chemical reactions and phenomena upon which LÜPPO-CRAMER founded the above-mentioned conclusion, can even be accounted for in a simpler way by assuming that the subhaloids are chemically defined compounds, so that it has not yet been proved that it is correct to deny the existence of silver subhaloids. K. SCHAUM [15]), too, has pointed out that the direct photo-chemical product of decomposition of silver bromide cannot be silver, for if silver bromide is exposed to light by the side of bright, metallic silver, Ag Br becomes dark, but at the same time the silver assumes a violet colour; "es ist thermodynamisch unmöglich, dass in dem nämlichen Systeme gleichzeitig AgBr in Ag und Ag in AgBr übergeht". Hereby it was proved, not only that the conception of the silver subhaloid as an absorption compound, was untenable, but also that the formula of the stable silver haloid could not possibly be Ag Hal, but must be $Ag_n\,Hal_n$, in which n is a figure as yet unknown.

Quite independently of K. Schaum I 16) have arrived at the same result by the explanation of a few developing phenomena in the case of exposed silver haloid free from binding substance.

Let us indicate the sensitiveness to light of a substance generally by placing the letter l before the name of it, thus:

$$l\,\mathrm{AgJ} > l\,\mathrm{AgBr}$$

This is also applicable to the substance of the latent image, the α silver subhaloid:

$$l\,\mathrm{Ag_nJ_{n-a}} > l\,\mathrm{Ag_nBr_{n-a}}.$$

Now the remarkable case may occur that *seemingly*

$$l\,(\mathrm{AgJ\ AgBr}) > \left\{\begin{array}{c} l\,\mathrm{AgJ} \\ \text{and} \\ l\,\mathrm{AgBr} \end{array}\right.$$

i.e. the *reducibleness*, which is pretty generally erroneously identified with sensitiveness, increases by exposure more rapidly in the case of iodide silver bromide than in the case of silver iodide or of silver bromide.

This is to be accounted for by the circumstance that iodide silver bromide produces a substance of the latent image less sensitive to light than is yielded by silver iodide, while at the same time this substance is formed more rapidly than by silver bromide, in other words, while at the same time iodide silver bromide is really more sensitive to light than silver bromide. In the most favourable case the latent image may consist of $Ag_n\,Br_{n-a}$. As iodide silver bromide was obtained from the synthesis of the subbromide with iodine, it follows that the formula of the silver bihaloid must be $Ag_n\,Br_{n-a}J_a$. On the analogy of this $Ag_n\,Br_n$, is obtained, if bromine is taken instead of iodine, so that the general formula of silver haloid becomes $Ag_n\,Hal_n$.

If we now assume that the photo-chemical decomposition of silver haloid, resp. subhaloid, again and again forms a new subhaloid, each time by the loss of one halogen atom, we obtain the following series:

$$\mathrm{Ag_nHal_n \rightarrow Ag_nHal_{n-1} \rightarrow Ag_nHal_{n-2} \rightarrow \ldots \rightarrow Ag_nHal_2 \rightarrow Ag_nHal \rightarrow nAg}\ . \quad (I)$$

it being, of course, not impossible that one or more of these subhaloids do not exist.

R. Luther 17) observed no difference between the oxidation potentials of the subhaloids of the latent and of the visible photo-chemical decompositions, and therefore assumed the formation of the same subhaloid in both cases. In order to determine the chemical composition of this subhaloid, he added at intervals to a known quantity of silver a chlorine solution containing $^1/_{10}$ of the quantity required for the formation of $AgCl$, and then each time determined electromotorically the oxidation potential of the remaining chlorine. In the beginning it remained constant at 0,55 Volts, but when the composition Ag_2Cl had been reached, it suddenly became 1,45 Volts, and after that remained fairly constant. In the synthesis of silver bromide he also observed a rise of the potential at Ag_2Br. E. BAUER[18]) confirmed this in the case of Ag_2Cl, and could further demonstrate a slight rise of the potential in proportion as the percentage of chlorine increased, from which he inferred that Ag_2Cl forms with silver chloride homogeneous mixture series (absorption compounds). On the ground of the existence of a number of subhaloids it follows from this just as well that the subhaloids with an increasing amount of halogen show a very slight rise of the oxidation potential without there being any need to deny the formation of absorption compounds of these subhaloids with silver haloid. At the same time it appears that for the present a more exact determination of these subhaloids by this method does not promise much success.

If, however, these results are considered in connection with series (I), it appears that the first subhaloid formed synthetically, and consequent poorest in halogen, is Ag_2Hal, and the following improved photo-chemical decomposition series is obtained:

$$Ag_{2n}Hal_{2n} \rightarrow Ag_{2n}Hal_{2n-1} \rightarrow Ag_{2n}Hal_{2n-2} \rightarrow \ldots \rightarrow$$
$$\rightarrow Ag_{2n}Hal_{n+1} \rightarrow Ag_{2n}Hal_{n} \rightarrow 2nAg \quad (II)$$

This series is in harmony with the opinion already expressed by J. M. EDER[19]) some time ago: "Vielleicht bilden sich auch Silbersubchloride, welche als Zwischenprodukte von Ag_2Cl und $AgCl$ aufzufassen sind."

One of the most prominent peculiarities of the silver subhaloids, by which they were even discovered, is their absorption spectrum. As these subhaloids have the power of rendering the whole visible spectrum (the subchlorides do this best of all), I have endeavoured to determine experimentally the colour sequence of series (II).

Method of Investigation.

The method of procedure might have consisted in photographing the sun's spectrum by the SEEBECK process and in subsequently controlling the colour changes by means of a sun spectrum placed crosswise. If e. g. the red subhaloid originates after the green, the latter will have the power of yielding the red subhaloid, but it will never be possible for the green subhaloid to be photo-chemically formed out of the red subhaloid. This experiment already made by O. WIENER[20]) yields: 1st, doubtful results, because the primary rendering of the spectrum already leaves much to be desired, and this is, consequently much more the case with the secondary rendering; 2nd, unreliable results, because in this way the chemically pure subhaloid is never experimented with, but by the side of it there is always an admixture of silver haloid. It is true, the POITEVIN process yields a better colour rendering, but the results are not any more reliable, because, as LÜPPO-CRAMER[21]) has proved, in this process photo-oxidation takes places by the side of photo-reduction. I, therefore, selected another method.

According to H. LUGGIN[22]) and R. LUTHER[23]) the photo-chemical decomposition of silver haloids in a closed space gets with a definite light intensity into a state of equilibrium owing to the halogen pressure which sets in. GUNTZ[24]) determined the equilibrium pressure with various light intensities by exposing silver chloride under different, known chlorine pressures, in small glass tubes sealed in a blowpipe flame. This method produces decomposition in these tubes, in which the pressure is too small for the state of equilibrium, but is not suitable for determining the colour sequence, because the colour of the subhaloid can only be observed through that of the halogen, consequently very inaccurately. Therefore it is better to proceed as follows.

If silver haloid is emulsionized in a binding substance (one might also say: "if it is placed in a half-closed space") the photo-chemically liberated halogen cannot escape immediately, but with a definite light intensity a halogen pressure D per unit of time will set in, which is dependent upon the halogen pressure D_1 which the photo-chemical decomposition process would produce, diminished in the first place by the pressure D_2 which is lost by diffusion, and in the second place by the pressure D_3 which is lost by the chemical combination with a halogen absorbent (chemical sensitizer).

$$D = D_1 - (D_2 + D_3) \quad . \quad . \quad . \quad . \quad . \quad . \quad (III)$$

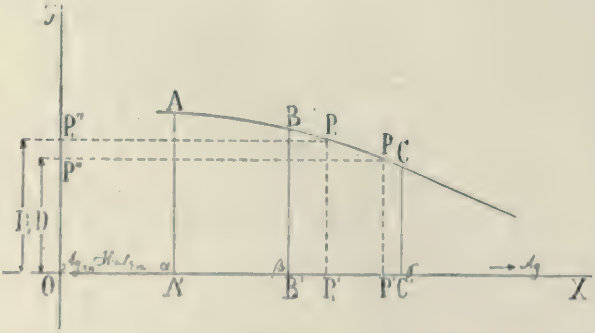
In this formula D_2 and D_3 in the second member, and consequently D too, may be modified.

Now seeing that a rise of halogen pressure is accompanied by an increase of diffusion and of the rapidity of reaction of chemical combination, a fairly constant halogen pressure may continue to exist for a definite period during the decomposition, if the chemical sensitizer is present in not too small a quantity. (Compare the result of the experimental inquiry into the influence of the size of the grain upon *D*, below, with the accuracy of this reasoning). Practically it is not even so very simple to take too small a quantity of chemical sensitizer, because the first visible decomposition of the silver haloid already sets in, when a quantity of halogen, too small to be weighed, has been photo-chemically liberated, which is undoubtedly owing to the intense colour of the subhaloids.

The cause of the more rapid photo-chemical decomposition of silver haloid in the presence of a chemical sensitizer has been attributed by GUNTZ [25]) to the development of heat, which accompanies the chemical combination of the liberated halogen, because this photo-chemical decomposition is attended with heat absorption. If this cause really had such a great influence upon the decomposition process, formula (III) would have to be considerably modified. This, however, is not the case. LÜPPO-CRAMER [26]) has demonstrated experimentally that the chemical sensitizer only accelerates the decomposition process, if the silver haloid is emulsionized. Silver haloid precipitated in a test tube does not show a trace of accelerated photo-chemical decomposition, neither by the addition of silver nitrate, nor by the addition of ammonia. I must, however, observe that the colours which appear are not the same. Consequently the thermic influence of the chemical sensitizer, referred to by GUNTZ, is so small that in practice it may be ignored, and may at most be taken as a theoretical correction of formula (III), especially if it is borne in mind that the total amount of halogen that is liberated and reacts in my experiments, is extremely small.

On the analogy of the more or less regular changes of properties in the case of other chemical series, as e. g. the fatty acids, it may be assumed that the subhaloids according to series (II) will show an increased or decreased affinity, however small the differences may be mutually. As with a constant light intensity the photo-chemical decomposition of the subhaloid gets, at a certain definite halogen pressure, into a state of equilibrium, we may say that the equilibrium pressure in the case of the subhaloids according to series (II) undergoes an increase or a decrease. Even the measurements of E. BAUER [27]) mentioned before, who observed a rise of the potential with a higher proportion of halogen, point to the fact that with a constant light intensity this equilibrium pressure will decrease if the amount of halogen in the subhaloids is smaller.

If now formula (III), in which, consequently, *D* is practically constant for some time, is applied to the assumed subhaloids $\alpha, \beta, \gamma \ldots$, in which each subsequent subhaloid is poorer in halogen than the preceding one, and which with the same light intensity have respectively the equilibrium pressure $D_\alpha, D_\beta, D_\gamma, \ldots\ldots$ then we get $D_\alpha > D_\beta > D_\gamma > \ldots\ldots\ldots$ If $D = D_\beta$, then the photo-chemical equilibrium will set in with the β subhaloid, recognizable by the colour of this subhaloid, that is to say, the photo-chemical decomposition does continue through the loss of halogen, but the state of decomposition will not proceed *beyond* the β subhaloid, as long as D_β does not decrease. Thus first a definite colour is seen to constantly increase with the photo-chemical decomposition till a maximum has been reached, after which, sometimes after a very long exposure, a change of colour becomes noticeable. In the case of $D_\beta > D > D_\gamma$ a blend of the colours of the β and the γ subhaloid will appear. Consequently, by giving to D a higher or a lower value, we have it in our power to determine the colour sequence of the subhaloid according to (II); by decreasing the quantity of chemical sensitizer or by preventing diffusion, subhaloids richer in halogen, in the opposite case subhaloids poorer in halogen are obtained.



The graphic representation clearly shows this. If on the abscissa (see fig.) at mutually equidistant points A', B', C', ... we indicate the subhaloids $\alpha, \beta, \gamma, \ldots\ldots$ in equal molecular quantities, and on the ordinate the equilibrium pressures $A'A$, $B'B$, $C'C, \ldots$, corresponding to them with a definite light intensity, then the connection of the points $A, B, C, \ldots$ must yield a line which approaches the abscissa from O in a positive direction. If we assume now that the amount of one of the subhaloids, say β, decreases in such a way from B both in the positive and the negative direction on the abscissa, that at $\frac{1}{n}$ of the distance from B' to A' or C' there is the

$\frac{n-1}{1}$ th part of the quantity of β subhaloid (which is in B'), then the quantity of β' subhaloid will be zero both in A' and in C'. If now we further assume the same distribution in the case of the other subhaloids, then beginning at the point O, a series of colours will successively appear on the abscissa, among which there are mixed colours composed of at most two components between the points $A', B', C' \ldots .$ The equilibrium pressure at any point is then determined by the ordinate from this point to the intersection with the line $ABC \ldots$ Suppose that with the photo-chemical decomposition a constant halogen pressure $D = OP''$ prevails, then the state of decomposition will not progress beyond P', because the equilibrium pressure $P'P$ corresponding to P' is equal to OP''. Consequently in P' a mixture of the β and γ subhaloids will appear, the quantities of which are determined by the proportion $N_\beta : N_\gamma = P'C' : P'B'$. A mixed colour will then appear, in which, according to the figure, the colour of the β subhaloid will be predominant. If D becomes greater, say $D' = OP_1''$, then the state of equilibrium will set in at P_1', where, according to the figure, the colour of the β subhaloid is predominant. Now by slightly modifying D between the equilibrium pressures of two photo-chemically consecutive subhaloids, it must be possible to obtain all transitional tints from one subhaloid to another, and this could actually be demonstrated in all those cases in which it was experimentally possible.

To obtain these results, the subhaloids must, of course, be sufficiently sensitive to light. Still with a few experiments, as those with subiodides and subbromides, phenomena are observed which cannot be accounted for as yet, and require further, separate investigation. We shall not enter into them here.

From the graphical representation it further appears that D can never become greater than the highest position of the line $ABC \ldots$ above the abscissa. If D is smaller than the equilibrium pressure of the subhaloid poorest in halogen, then silver begins to separate out photo-chemically.

If we assume that the line $ABC \ldots$ is continued still further towards the Y-axis, i.e. that the silver haloid is placed in O before the α subhaloid on the abscissa, then the ordinate belonging to it will correspond to the lowest halogen pressure at which the photochemical decomposition of silver haloid still takes place with this light intensity, and which answers to the above-mentioned chlorine pressure determinations by GUNTZ.

Now suppose these results to be incorrect, because the continuation of $ABC \ldots \parallel OX$, or from O onward recedes in positive direction from the abscissa, then it will never be possible to obtain by varying (D_2+D_3) the colour of one or two of the subhaloids, but the photo-chemical decomposition will always progress more or less rapidly in the same way in all cases. However, the results of the experiments mentioned below cannot be reconciled to this supposition.

The influence of the size of the grain. As the photo-chemical decomposition of silver haloids is restricted to the surface of the grains, it is easy to understand that the size of the grain must influence the decomposition process. The finer the grain, the more "saturated" the colour, the coarser the grain, the weaker the colour will be. As in formula (III) D becomes greater owing to the finer grain, D_2 and D_3 will therefore also increase. Consequently by exposing coarser and finer silver haloid grains emulsionized under as much as possible the same circumstances, it can be determined experimentally, to what extent D changes through an increase of D_1, and an increase of (D_2+D_3) depending upon it. I have made this experiment with a fine-grain silver chloride gelatine emulsion, and silver chloride gel emulsionized in gelatine, but found, except in the saturation of the colours, a very small difference, which might even be put down to an inaccuracy in the experiment, viz. a slight difference in the amount of chemical sensitizer.

Control. If in formula (III) D_3 is made smaller, D will become greater, and the colour of a subhaloid richer in halogen will appear. The same thing may, however, be obtained in another way. The equilibrium pressure is smaller with a weaker light intensity (approaches zero in the dark), but in this case D_1 will also decrease a well as the term (D_2+D_3) dependent upon it, and, as has been shown by the enquiry into the influence of the size of the grain upon silver haloid, D thereby changes little or nothing. The consequence of making the photo-chemical decomposition take place with a smaller light intensity, will therefore consist in the appearance of subhaloids richer in halogen. Therefore, by lowering D as well as the light intensity, the same subhaloids richer in halogen, in the opposite case the same subhaloids poorer in halogen, will be seen to appear.

Another means of control is afforded by increasing D after the photo-chemical decomposition has been interrupted by introducing halogen into the preparation; in this case the same subhaloids richer in halogen must be obtained back again. This method, however, has the drawback, that owing to the absorption spectrum of the halogen, the colours of the subhaloids are to be observed in a less pure condition.

The colour value. Seeing that side by side with the subhaloid we always have the coloured halogen, although in a less than equivalent quantity, the colours of the subhaloids will never appear so clearly as in the case of the preparations prepared chemically by M. CAREY LEA'S and LÜPPO-CRAMER'S[28]) method.

The place of the α-subhaloid. My investigations as to the substance of the latent image[29]) and its preparation[30]) show that in the case of iodide as well as of bromide and chloride the α-subhaloid has a green colour. As the assumption of a subhaloid still richer in halogen to account for BUNSEN-ROSCOE'S photo-chemical induction[31]) and for auto-sensitation[32]) is superfluous, I have attempted to trace this possibly extant subhaloid by the photo-chemical method indicated. If silver bromide with an excess of potassium bromide is made to precipitate from a silver nitrate solution, dried, and exposed under carbon tetrachloride to moderately strong daylight, it soon begins to show a green colour. In this preparation the diffusion of the liberated halogen is extremely slight, and potassium bromide is a very weak chemical sensitizer, with which the reaction product KBr_3 with the subhaloid partially shows a reversed reaction in the dark. Under these circumstances the α-subbromide is, therefore, obtained photo-chemically in visible quantities, and hitherto this has been the simplest method found by me of preparing light-proof preparations from this substance. The halogen pressure can, however, be increased still more by omitting this weak chemical sensitation as well. In a dry, pure collodion coating pure silver bromide yielded a grey discoloration with the lowest light intensity with which decomposition is still to be observed. In the dark the light yellow silver bromide appeared again after some time; consequently an almost complete re-formation of the silver bromide takes place, from which it may be inferred that the loss of bromine has been reduced to a minimum, and the subhaloid richest in halogen may have appeared with the photo-chemical decomposition in a visible quantity. But even now the grey colour need not be attributed to a subhaloid richer in halogen than the α-subhaloid, for the equivalent amount of bromium may mix its brownish red colours with the green of the α-subbromide so as to yield grey. As, therefore, the green α-subhaloid is to be considered the one richest in halogen we know at present, we may say *that every other colour must be ascribed to a subhaloid poorer in halogen.*

Use of the α subhaloid. If in these experiments we start from the green α-subhaloid instead of from silver haloid, a *different* sequence of colours is obtained. With silver nitrate the green preparation very rapidly turns grey or black through the formation of mixed colours with the subhaloids poorer in halogen, and with the exception of a single case mentioned below, it is therefore unfit for controlling purposes. So the best plan is to start from silver haloid only, which owing to its white or light yellow colour has little or no influence upon the colour of the subhaloids that are formed.

The binding substance. In most cases gelatine was used for this purpose. In a perfectly dry condition it does not absorb free halogen; it does, however, in the presence of water.

The chemical sensitizers. As it appeared desirable to me, in connection with these experiments, to obtain as much as possible results that could be compared with each other, I have made as little as possible use of different chemical sensitizers. Besides alkali-haloid and moist gelatine, silver nitrate was selected as being a powerful sensitizer. The photo-chemical reduction in the presence of gelatine has, as appeared from a parallel experiment without silver haloid, no disturbing influence upon the determination of the colours of the subhaloids.

Description of the experiments.

The silver subiodides. The cause why hitherto nobody has succeeded in demonstrating the iodine liberated photo-chemically, is no doubt to be put down to the very unfavourable conditions of diffusion (high atomic weight and low vapour tension of iodine), and to absorption by silver iodide with the formation of an absorption compound 33)). Moreover the visible photo-chemical decomposition is always very slight, notwithstanding the high sensitiveness of silver (sub)iodide, to which I have already referred more than once, in other words, only very little iodine is liberated, which has been associated by H. LUGGIN 34)) with the low equilibrium potential of silver iodide. This makes silver iodide together with iodo-silver bromide, mentioned above, the most suitable silver haloids for daguerreotypy, in which the destruction of the α-subhaloïd, upon which the reducibleness depends, would otherwise be much stronger as compared with the emulsion processes. Consequently it is unnecessary to emulsionize the silver iodide.

If silver iodide with an excess of potassium iodide is precipitated from a silver nitrate solution, then a very slight discoloration appears on exposure 35)), without a subiodide colour becoming observable. The cause is probably that during the precipitatien of silver iodide potassium iodide is separated out as well. Now in photo-chemical decomposition the liberated iodine is absorbed in a less degree by silver iodide, but largely by potassium iodide, potassium tri-iodide being formed, which with subiodide gets into a state of photo-chemical equilibrium, which is nearer to silver iodide than that of subiodide and adsorbed iodine. The sensitiveness of potassium iodide, by which iodine is photo-chemically liberated, may also have some influence.

If silver iodide with an excess of silver nitrate be precipitated by potassium iodide, it is free from potassium iodide. The photo-chemical decomposition now proceeds much further; a greyish green colour sets in, which points to a high amount of α-subiodide. This seems at variance with the observations of HERSCHEL's effect, and the solarisation in the case of the silver iodide daguerreotype plate, where with much shorter exposures a decrease of reducibleness undoubtedly sets in, owing to the photo-chemical splitting up of α-subiodide into β-subiodide and iodine. This contradiction is solved, if it is borne in mind that, to render the exposed silver haloid reducible, the presence of the α-subhaloid alone is not sufficient, but that, moreover, it must be at the surface of the silver haloid, so that through molecular attraction the reduction products of the dissolved silver salt or the mercury vapour may be able to settle on it. The greyish green discoloration may, therefore, be attributable to a high amount of α-subiodide, but it may itself be covered by an extremely thin layer of subiodide poorer in halogen.

If we endeavour to remove the halogen pressure of iodine altogether by conducting the photo-chemical decomposition under a silver nitrate solution, then the reductions become very complicated. The acceleration of the visible photo-chemical decomposition appears to be hardly appreciable, while the substance assumes a grey colour, and yet in the silver iodide collodion process silver nitrate behaves as an excellent chemical sensitizer. On a former occasion [36]) I already pointed out that *in the light* silver nitrate must exercise a strongly oxidizing influence upon subiodide, silver oxide being formed, and accounted for the more rapid increase in the reducibleness (i.e. more rapid rise of the amount of α-subiodide) by this oxidation, which can act only then in such a way that β-subiodide is more rapidly oxidized into α-subiodide than the latter into silver iodide. Consequently when silver iodide in a silver nitrate solution is exposed, two opposite actions take place: a progressive reaction, the photo-chemical decomposition, and a regressive reaction, the oxidation, the former taking place a little more rapidly than the latter, which reactions probably even with the subiodides poorer in halogen perfectly neutralize each other. With oxidation, however, silver oxide is separated out; I therefore surmise that the grey discoloration mentioned before must be ascribed to this silver oxide.

This photo-chemical decomposition might consequently be accelerated 1st by taking an iodide more sensitive to light, and 2nd by decreasing the oxidation by silver nitrate (exposure with smaller light intensity). Both these conditions have been complied with in the extremely rapid photo-chemical decomposition of *α*-subiodide in weak twilight observed by me[37]).

Beside these reactions others set in, as the probable formation of iodates, oxidation through one of the reaction products of the chemical binding of iodine and silver nitrate, etc., the investigations into which are partly incomplete as yet.

As subbromides and subchlorides oxidize far less rapidly, as is well-known, the deviations occurring in the case of subiodides, are much less likely to occur with them.

Further a red subiodide of M. CAREY LEA[38]) is well known, which, consequently, must contain a smaller amount of halogen than *α*-subiodide.

Of the colour sequence of series (II) we accordingly know only

green, ... red, ... (IV)

The silver subbromides. In the following table the observations have been arranged in such a way, that D constantly increases.

$Ag_{2n}\ Br_{2n}$ Fine-grained. In gelatine.	Discoloration in daylight (October, 11 to 2 o'clock)
(1). with 10°/$_0$ aqueous $AgNO_3$ sol.	yellowish, reddish or brownish violet
(2). with much H_2O	brownish violet
(3). with little H_2O	red
(4). moist	reddish violet
(5). less moist	bluish violet
(6). dry	bluish
Without binding substance	
(7). with KBr under ether, CCl_4	green

These discolorations were not observed simultaneously, but always when the colour was most intense without passing into another. The decomposition takes place so unequally that, when exposed simultaneously, (1) and (2) already have a clearly perceptible colour after a few tens of seconds, whilst the others show hardly any visible decomposition. Compared with each other, the latter preparations show little difference in the rapidity with which the colours appear. We see here a deviation from LÜPPO-CRAMER's observation referred to above, that photo-chemical decomposition is accelerated by chemical sensitation only in an emulsion.

If in the case of preparation (7) the ether or carbon tetrachloride is allowed to evaporate in the dark room after exposure, then the bromine is liberated, which is distinctly perceptible by its smell and the potassium iodide starch reaction.

Between the preparations (3), (4), (5) and (6) all intermediate tints from blue to red could be obtained by increase oı decrease of the amount of water.

The preparations (6) and (7) still contain a trace of adsorbed water.

With the very rapid photo chemical decomposition already referred to, the preparations (1) and (2) show the violet colour anew. This may be accounted for by the fact that D was so small, that no constant equilibrium pressure was to be reached in the photo-chemical decomposition series.

When the experiment was repeated a number of times, preparation (1) showed a different colour each time, probably through changes in D and the light intensity. In direct sunlight especially the yellowish brown colour appears; sometimes it was even blue-black through the silver separated out. The yellowish brown mixed colour points to the formation of a yellow subbromide with the ultimate products.

Tests have been made by observing the same photo-chemical decomposition with weaker light intensities. Then (2) yielded a red colour, and (3), (4) and (5) showed a distinct shifting of the colour towards blue. Preparation (7) assumed a greyish green colour in direct sunlight. Further the red preparation rapidly developed a blue colour in bromine water, which colour then entirely bleached into silver bromide, without my being able to observe the green subbromide with certainty. Of the green, blue, and red preparations, the size of the grain being the same, and free from binding substance, the red one reacted most rapidly upon sodium thiosulphate, H_2CrO_4, HNO_3 and $(NH_4)_2S_2O_8$, and especially the green preparation showed considerable resistance. By putting the α-subbromide in a neutral 10 % sodium thiosulphate solution I was able, even by the light in the room, to observe distinctly a colour change through bluish green to blue.

The colour sequence of series II is consequently in the case of subbromides:

green, bluish green, blue, violet, red, . . . yellow. . . . . . (V)

The silver subchlorides. In the following table the same arrangement has been observed as in the case of the subbromides.

Ag_{2n} Cl_{2n} Very fine grain	Discoloration in daylight (October 11 to 2 o'clock)
In gelatine.	
(1) with 10 % aqueous $AgNO_3$ sol.	reddish orange
(2) with $AgNO_3$ dry	red.
(3) with NH_4Cl moist	violet.
(4) with NH_4Cl dry	blue.
Without binding substance.	
(5) with NH_4Cl under CCl_4	bluish green.

By variation the amount of water all intermediate tints can be obtained between preparations (3) and (4), while by decrease of the amount of $AgNO_3$ preparation (2) becomes reddish violet to violet, and has for this reason been placed before (3).

The preparations (2), (4) and (5) still contain a trace of adsorbed water.

In Poitevin's photochromics there also occurs a yellow (more orange-like) subchloride. Preparation (1) already yields a colour which inclines from red to yellow; therefore the yellow subchloride is probably formed after the red. In direct sunlight this preparation assumed a yellow colour. However, I found no indications that this was a subchloride, for neither in ammonia nor in a 10 % sodium thiosulphate solution did it undergo any perceptible change, while the red and the reddish orange preparation became yellow and yellowish brown in these two solutions. So it may just as well be photo-chemically formed collodial silver. However, the yellow subchloride cannot be classed anywhere between or before the other colours. In analogy with what is similar in the case of the subbromides it may therefore be assumed, that after all, it comes after the reddish orange preparation.

The green *α* subchloride is known to be the subchloride richest in halogen, and preparation (5) already inclines to it, so that in the case of the subchlorides the colour sequence of series (II) is

green, bluish green, blue, violet, red, orange, yellow . . . (VI)

The silver subfluorides. Silver fluoride is hygroscopic and too insensible to light for these experiments. Still there is a yellow subfluoride of Guntz 39) with the formula Ag_2Fl.

The silver subcyanides. Their existence is still doubtful. A chemically pure silver cyanide preparation of E. de Haën, showed the same bluish violet discoloration both without and with a binding substance, and even under CCl_4. In the case of silver cyanide the photo-chemical decomposition therefore takes place according to other laws than with the foregoing silver (sub)haloids.

The silver subrhodanides. Their existence, too, is still doubtful. On account of its very slight sensitiveness to light silver sulphocyanide is unsuitable for these experiments.

Results and conclusions.

Let us now return to E. BAUER's modification theory, already referred to before, which owes its origin to the assumption of the existence of only one subhaloid, which view at one time obtained universally. As has been demonstrated experimentally, new colours only arise consecutively, if D decreases, in other words, if more halogen is liberated photo-chemically. Every new colour, therefore, belongs to a subhaloid poorer in halogen. The modification theory is not to be associated with this, and the assumption adopted of ascribing a definite absorption spectrum to each subhaloid, can still hold good.

If we compare the colours series (V) and (VI), we see that even with the exception of the place of the yellow subhaloid, which has not yet been fixed with absolute certainty, they show the same sequence of colours, while series (IV), as far as it is known, runs parallel with it. If we now bear in mind that, barring slight variations, the α-subhaloid is green, both with subiodide and subbromide and subchloride, we may account for the parallelism of the colour series by the fact that *subhaloids of analogous composition have analogous absorption spectra.*

The colour sequence itself, too, shows regularity: *the colours of the silver subhaloids,* arranged according to the photo-chemical decomposition series, follow NIETSKI's rule, in which halogen behaves like a bathochromic group, in other words, *with the decrease of the molecular weight of the silver subhaloids the maximum of the absorption spectrum is shifted from red to violet.* Although the structure formulae of the silver subhaloids are still unknown, it may be inferred from this that they all contain the group Ag_{2n} Hal_n, which behaves like a chromophore or contains it. *The cause of the sensitiveness to light of the silver subhaloids is, therefore, to be relegated to electro-magnetic light resonance.*

As according to NIETSKI's rule the maximum of the absorption spectrum of a subhaloid still richer in halogen than the α-subhaloid must be situated in the infra-red, and may therefore be colourless, the above-mentioned experiment for the detection of this subhaloid by increasing D appears to be perfectly worthless. Still this does not alter the conclusion drawn from this experiment, that every other colour than green appearing in photo-chemical decomposition is to be attributed to a subhaloid poorer in halogen.

If this subhaloid actually existed, it would have to have, in analogy with the other silver subhaloids, a maximum sensitiveness to light in the infra-red in accordance with its absorption spectrum. It would then have to make its influence strongly felt in spectrum photography, if the silver haloid plate previously received an exposure below its liminal value. H. Lehmann 40) in his experiments as to the infra-red spectra of alkali metals has actually observed that through a previous exposure and an ammonia bath a highly sensitive silver bromide gelatine plate increases its sensitiveness via *A* into the infra-red near Fraunhofer's line *Z*, but, and this is the great point, a *conspicuous* rise of sensitiveness in the infra-red appears nowhere from his experiments. Consequently what H. Lehmann observed was nothing else than the well-known auto-sensitation of the plate. So we may say that a subhaloid richer in halogen than the α-subhaloid does not exist.

According to Nietski's rule silver haloid would have to take the place of the colourless subhaloid assumed above, but it shows the deviation that the maximum of its absorption spectrum is not situated in the infra-red, but in the blue or violet, i.e. where the number of vibrations is about twice as high. *Consequently in the case of silver haloid, too, the cause of the sensitiveness to light is to be relegated to electro-magnetic light resonance.*

In the synthesis of silver haloid from silver and halogen, through the series of subhaloids, the electro-magnetic resonator undergoes changes which show a striking resemblance to the following well known phenomenon in acoustics. If we take a small, thin bar with a fixed and a detached end, it will resound at a tone corresponding to its key-note; by constantly lengthening this bar, the key-note is lowered, and the resonance will set in at a lower number of vibrations, until, after it has reached its maximum length, the next lengthening will at the same time fix the detached end, by which the key-note will get one octave higher, and accordingly the resonance will set in at the double number of vibrations.

Nietski's rule points to a yellowish green subhaloid as a subhaloid still poorer in halogen than the yellow one. In numerous experiments repeated under various circumstances, by endeavouring to keep *D* low and constant, I have not been able to observe a trace of it. It is true, the appearance of the mixed colours of the subhaloids poorest in halogen points to the formation of a yellow subhaloid as the last one formed photo-chemically. Consequently the formula $Ag_{2n}\ Hal_n$ may be assigned to it.

In the simplest case all the colours that appear, inclusive of the green of the α-subhaloid, may be reduced to 4 different ones, with the subhaloids belonging to them. If these subhaloids are indicated by the letters α, β, γ, and δ respectively, then series (II) becomes:

$$Ag_{2n}Hal_{2n} \rightarrow Ag_{2n}Hal_{2n-1} \rightarrow Ag_{2n}Hal_{2n-2} \rightarrow Ag_{2n}Hal_{2n-3} \rightarrow Ag_{2n}Hal_{2n-4} \rightarrow 2nAg. \text{(VII)}$$

α-subhal. β-subhal. γ-subhal. δ-subhal.
(green) (blue) (red) (yellow).

in which

$$Ag_{2n}\ Hal_{2n-4} = Ag_{2n}\ Hal_{n}$$

or

$$2n-4 = n$$
$$n = 4$$

so that series (VII) becomes:

$$Ag_8\ Hal_8 \rightarrow Ag_8\ Hal_7 \rightarrow Ag_8\ Hal_6 \rightarrow Ag_8\ Hal_5 \rightarrow Ag_8\ Hal_4 \rightarrow 8Ag.$$

α-subhal. β-subhal. γ-subhal. δ-subhal.
(green) (blue) (red) (yellow)

To summarize we may place the different subhaloids in the following table, in which Guntz's *solid* subfluoride may very well be classed.

subhaloid	subiodide	subbromide	subchloride	subfluoride
α-(green)	Ag_8J_7	Ag_8Br_7	Ag_8Cl_7	unknown
β-(blue)	Ag_8J_6	Ag_8Br_6	Ag_8Cl_6	,,
γ-(red)	Ag_8J_5	Ag_8Br_5	Ag_8Cl_5	,,
δ-(yellow)	unknown	Ag_8Br_4	Ag_8Cl_4	Ag_8Fl_4

The β-subiodide (Ag_8J_6) has been inserted in this table, because the solarization and Herschel's effect in the case of silver iodide plates point to the existence of this subiodide.

In conclusion I wish to point out that I [41]) have only partly succeeded in observing the high sensitiveness to light of the α-subiodide. The grey discoloration of the green preparation, which, as was shown by the sodium thiosulphate reaction, is caused rather by silver-oxide than by subiodides poorer in halogen, resp. silver, can hardly be ascribed to the formation of the blue β-subiodide, but may be put down to the formation of the red γ-subiodide.

If moreover, the regressive reaction by oxidation is taken into account, which, it is true, is less than in full daylight, but all the same has not been neutralized, the α-subiodide appears to be still far more sensitive to light than described by me.

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Mathematics. — *"An integral-theorem of* GEGENBAUER." By Prof. KLUYVER.

(Communicated in the meeting of February 27, 1909).

GEGENBAUER has proved a theorem according to which the product of two functions of BESSEL $J^{\nu}(ax)$ and $J^{\nu}(bx)$ with the same parameter $\nu > -\frac{1}{2}$ can be given the form of a definite integral [1]).

In a former communication [2]) I have applied this theorem for the case $\nu = 0$ when reducing some discontinuous integrals containing functions of BESSEL. I shall now give in the following a direct proof of the indicated theorem and shall use it to extend former results.

1. In order to find the product of two functions of BESSEL

$$J^{\nu}(ax) = \left(\frac{ax}{2}\right)^{\nu} \sum_{h=0}^{h=\infty} \frac{(-1)^h \left(\frac{ax}{2}\right)^{2h}}{h!\,\Gamma(\nu+h+1)},$$

$$J^{\nu}(bx) = \left(\frac{bx}{2}\right)^{\nu} \sum_{h=0}^{h=\infty} \frac{(-1)^h \left(\frac{bx}{2}\right)^{2h}}{h!\,\Gamma(\nu+h+1)}$$

we can multiply the absolutely converging power series. It is then evident, that (supposing $b < a$) we find for the coefficient of an arbitrary power of x a finite hypergeometic series with the fourth argument $\frac{b^2}{a^2}$.

We get [3])

$$J^{\nu}(ax)\,J^{\nu}(bx) = \left(\frac{abx^2}{4}\right)^{\nu} \sum_{h=0}^{h=\infty} \frac{(-1)^h \left(\frac{x}{2}\right)^{2h}}{h!\,\Gamma(\nu+1)\,\Gamma(\nu+h+1)} a^{2h} F\left(-\nu-h, -h, \nu+1, \frac{b^2}{a^2}\right).$$

To transform the hypergeometric series appearing here I shall use the notation of RIEMANN for the general hypergeometric function

$$P\left|\begin{matrix} a & b & c & \\ \alpha & \beta & \gamma, & z \\ \alpha' & \beta' & \gamma' & \end{matrix}\right|,$$

$$(\alpha + \alpha' + \beta + \beta' + \gamma + \gamma' = 1)$$

$$P_a^{\alpha} = (z-a)^{\alpha}\,[1 + A_1(z-a) + A_2(z-a)^2 + \ldots\ldots].$$

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[1]) NIELSEN. Handbuch der Theorie der Cylinderfunktionen, page 182.

[2]) Proceedings 1905.

[3]) NIELSEN. page 20.

It is then evident that for two of the singular points the differences of the exponents are equal, so that besides the ordinary substitution of order one also substitutions of order two as

$$P_1^{\beta}\left|\begin{matrix} 0 & -1 & +1 & \\ \alpha & \beta & \beta, & z \\ \alpha' & \beta' & \beta' & \end{matrix}\right| = 2^{-\beta} P_1^{\frac{\beta}{2}}\left|\begin{matrix} 0 & \infty & 1 & \\ \frac{\alpha}{2} & 0 & \beta, & z^2 \\ \frac{\alpha'}{2} & \frac{1}{2} & \beta' & \end{matrix}\right|$$

and

$$P_0^{\alpha}\left|\begin{matrix} 0 & -1 & +1 & \\ \alpha & \beta & \beta, & z \\ \alpha' & \beta' & \beta' & \end{matrix}\right| = P_0^{\frac{\alpha}{2}}\left|\begin{matrix} 0 & \infty & 1 & \\ \frac{\alpha}{2} & 0 & \beta, & z^2 \\ \frac{\alpha'}{2} & \frac{1}{2} & \beta' & \end{matrix}\right|$$

are possible.

The indicated reduction runs as follows:

$$F\left(-h, -v-h, v+1, \frac{b^2}{a^2}\right) = P_0^{0}\left|\begin{matrix} 0 & \infty & 0 & \\ 0 & -h & 1 & , \frac{b^2}{a^2} \\ -v & -v-h & 2v+1+2h & \end{matrix}\right| =$$

$$= \left(\frac{b}{a}\right)^h P_0^{-\frac{h}{2}}\left|\begin{matrix} 0 & \infty & 1 & \\ -\frac{h}{2} & -\frac{h}{2} & 0 & , \frac{b^2}{a^2} \\ -v-\frac{h}{2} & -v-\frac{h}{2} & 2v+1+2h & \end{matrix}\right| =$$

$$= 2^{\frac{h}{2}}\left(\frac{b}{a}\right)^h P_1^{-\frac{h}{2}}\left|\begin{matrix} 0 & -1 & +1 & \\ 0 & -\frac{h}{2} & -\frac{h}{2}, & \frac{a^2-b^2}{a^2+b^2} \\ 2v+1+2h & -v-\frac{h}{2} & -v-\frac{h}{2} & \end{matrix}\right| =$$

$$= 2^h\left(\frac{b}{a}\right)^h P_1^{-\frac{h}{2}}\left|\begin{matrix} 0 & \infty & 1 & \\ 0 & 0 & -\frac{h}{2} & , \left(\frac{a^2-b^2}{a^2+b^2}\right)^2 \\ v+\frac{1}{2}+h & \frac{1}{2} & -v-\frac{h}{2} & \end{matrix}\right| =$$

$$= 2^h \left(\frac{b}{a}\right)^h P_0^{\frac{h}{2}} \left| \begin{array}{cccc} 0 & \infty & 1 & \\ -\frac{h}{2} & 0 & 0 & , \frac{4a^2b^2}{(a^2+b^2)^2} \\ -\nu-\frac{h}{2} & \frac{1}{2} & \nu+\frac{1}{2}+h & \end{array} \right| =$$

$$= 2^h \left(\frac{b}{a}\right)^h P_0^{-h} \left| \begin{array}{cccc} 0 & -1 & +1 & \\ -h & 0 & 0 & , \frac{2ab}{a^2+b^2} \\ -2\nu-h & \nu+\frac{1}{2}+h & \nu+\frac{1}{2}+h & \end{array} \right| =$$

$$= \left(\frac{a+b}{a}\right)^{2h} P_0^0 \left| \begin{array}{cccc} 0 & -1 & 1 & \\ 0 & -h & 0 & , \frac{2ab}{a^2+b^2} \\ -2\nu & \nu+\frac{1}{2} & \nu+\frac{1}{2}+h & \end{array} \right| =$$

$$= \left(\frac{a+b}{a}\right)^{2h} P_0^0 \left| \begin{array}{cccc} 0 & \infty & 1 & \\ 0 & -h & 0 & , \frac{4ab}{(a+b)^2} \\ -2\nu & \nu+\frac{1}{2} & \nu+\frac{1}{2}+h & \end{array} \right| =$$

$$= \left(\frac{a}{a+b}\right)^{2h} F\left(-h,\ \nu+\tfrac{1}{2},\ 2\nu+1,\ \frac{4ab}{(a+b)^2}\right).$$

So finally we have

$$a^{2h} F\left(-h,\ -\nu-h,\ \nu+1.\ \frac{b^2}{a^2}\right) = (a+b)^{2h} F\left(-h,\ \nu+\tfrac{1}{2}.\ 2\nu+1,\ \frac{4ab}{(a+b)^2}\right),$$

a transformation given by GAUSS.

We now substitute for the just given hypergeometrical series the integral

$$\frac{2^{2\nu}\ \Gamma(\nu+1)}{\sqrt{\pi}\ \Gamma(\nu+\frac{1}{2})} \int_0^1 z^{\nu-\frac{1}{2}} (1-z)^{\nu-\frac{1}{2}} \left(1 - \frac{4ab}{(a+b)^2} z\right)^h dz,$$

and we find if in the integral we put $z = \cos^2 \frac{\varphi}{2}$

$$a^{2h} F\left(-h,\ -\nu-h,\ \nu+1,\ \frac{b^2}{a^2}\right) = \frac{\Gamma(\nu+1)}{\sqrt{\pi}\ \Gamma(\nu+\frac{1}{2})} \int_0^\pi (a^2+b^2-2ab\cos\varphi)^h \sin^{2\nu}\varphi\, d\varphi.$$

In the development found for the product $J^\nu(ax)\ J^\nu(bx)$ the above mentioned integral is introduced.

Putting

$$a^2 + b^2 - 2ab\cos\varphi = \Omega^2,$$

we obtain

$$J^\nu(ax)\,J^\nu bx = \frac{a^\nu b^\nu x^\nu}{2^\nu\sqrt{\pi}\;\Gamma(\nu+\frac{1}{2})}\int_0^\pi sin^{2\nu}\varphi\,d\varphi\left(\frac{x}{2}\right)^\nu\sum_{h=0}^{h=\infty}\frac{(-1)^h\left(\frac{\Omega x}{2}\right)^{2h}}{h!\;\Gamma(\nu+h+1)},$$

or

$$J^\nu(ax)\,J^\nu(bx) = \frac{a^\nu b^\nu x^\nu}{2^\nu\sqrt{\pi}\;\Gamma(\nu+\frac{1}{2})}\int_0^\pi \frac{J^\nu(\Omega x)}{\Omega^\nu}\,sin^{2\nu}\varphi\,d\varphi,$$

by which the indicated theorem of Gegenbauer has been proved.

2. With the aid of this theorem we can extend some well-known results concerning discontinuous integrals, in which functions of Bessel appear; particularly do the two following theorems[1])

$$\frac{c^{\nu+1}}{a^\nu}\int_0^\infty J^{\nu+1}(uc)\,J^\nu(ua)\,du = \begin{cases}1 & for\ a < c,\\ 0 & for\ a > c,\end{cases}$$

$$\frac{c^{\nu+2}}{a^\nu}\int_0^\infty J^{\nu+2}(uc)\,J^\nu(ua)\,\frac{du}{v} = \begin{cases}\frac{1}{2}(c^2-a^2) & for\ a < c,\\ 0 & for\ a > c.\end{cases}$$

lend themselves to this extension.

The theorem of Gegenbauer namely allows on the ground of these results to determine in certain supposition the value of the discontinuous integrals

$$W_1 = \frac{c^{\nu+1}}{a_1^\nu a_2^\nu\ldots a_n^\nu}\int_0^\infty J^{\nu+1}(uc)\,J^\nu(ua_1)\,J^\nu(ua_2)\ldots J^\nu(ua_n)\,\frac{du}{u^{\nu(n-1)}},$$

$$W_2 = \frac{c^{\nu+2}}{a_1^\nu a_2^\nu\ldots a_n^\nu}\int_0^\infty J^{\nu+2}(uc)\,J^\nu(ua_1)\,J^\nu(ua_2)\ldots J^\nu(ua_n)\,\frac{du}{n^{\nu(n-1)+1}},$$

in which the number of J-functions is arbitrary and ν is $> -\frac{1}{2}$.

Let us think the positive numbers $a_1, a_2, \ldots a_n$ to be successive sides of a broken line $OA_1A_2\ldots A_n$, let us put $\angle OA_kA_{k+1} = \varphi_k$ and $OA_k = s_k$, then we find successively

$$\frac{1}{a_1^\nu a_2^\nu u^\nu}\,J^\nu(ua_1)\,J^\nu(ua_2) = \frac{1}{2^\nu\sqrt{\pi}\;\Gamma(\nu+\frac{1}{2})}\int_0^\pi\frac{J^\nu(us_2)}{s_2^\nu}\,sin^{2\nu}\varphi_1\,d\varphi_1,$$

$$\frac{1}{s_2^\nu a_3^\nu u^\nu}\,J^\nu(us_2)\,J^\nu(ua_3) = \frac{1}{2^\nu\sqrt{\pi}\;\Gamma(\nu+\frac{1}{2})}\int_0^\pi\frac{J^\nu(us_3)}{s_3^\nu}\,sin^{2\nu}\varphi_2\,d\varphi_2,$$

. . . .

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[1]) Nielsen, p. 198.

$$\frac{1}{s^\nu_{n-1} a^\nu_n u^\nu} J^\nu(us_{n-1})\, J^\nu(ua_n) = \frac{1}{2^\nu \sqrt{\pi}\, \Gamma(\nu+\frac{1}{2})} \int_0^\pi \frac{J^\nu(us_n)}{s^\nu_n} \sin^{2\nu} \varphi_{n-1}\, d\varphi_{n-1}\,,$$

so that we get

$$W_1 = \frac{1}{[2^\nu \sqrt{\pi}\, \Gamma(\nu+\frac{1}{2})]^{n-1}} \int_0^\pi \sin^{2\nu}\varphi_1\, d\varphi_1 \int_0^\pi \sin^{2\nu}\varphi_2\, d\varphi_2 \ldots \int_0^\pi \sin^{2\nu}\varphi_{n-1}\, d\varphi_{n-1} \times$$

$$\times \frac{c^{\nu+1}}{s^\nu_n} \int_0^\infty J^{\nu+1}(uc)\, J^\nu(us_n)\, du,$$

$$W_2 = \frac{1}{[2^\nu \sqrt{\pi}\, \Gamma(\nu+\frac{1}{2})]^{n-1}} \int_0^\pi \sin^{2\nu}\varphi_1\, d\varphi_1 \int_0^\pi \sin^{2\nu}\varphi_2\, d\varphi_2 \ldots \int_0^\pi \sin^{2\nu}\varphi_{n-1}\, d\varphi_{n-1} \times$$

$$\times \frac{c^{\nu+2}}{s^\nu_n} \int_0^\infty J^{\nu+2}(uc)\, J^\nu(us_n) \frac{du}{u}.$$

Let now in the first place be

$$c > a_1 + a_2 + \ldots + a_n,$$

then c is certainly greater than s_n, and we find

$$W_1 = \left[\frac{1}{2^\nu \sqrt{\pi}\, \Gamma(\nu+\frac{1}{2})} \int_0^\pi \sin^{2\nu} \alpha\, d\alpha \right]^{n-1},$$

$$W_2 = \tfrac{1}{2}\,(c^2 - a_1^2 - a_2^2 \ldots - a^2_n) \left[\frac{1}{2^\nu \sqrt{\pi}\, \Gamma(\nu+\frac{1}{2})} \int_0^\pi \sin^{2\nu} \alpha\, d\alpha \right]^{n-1}.$$

As

$$\int_0^\pi \sin^{2\nu} \alpha\, d\alpha = \frac{\sqrt{\pi}\, \Gamma(\nu+\frac{1}{2})}{\Gamma(\nu+1)}$$

we find as final result

$$W_1 = \frac{c^{\nu+1}}{a^\nu_1 a^\nu_2 \ldots a^\nu_n} \int_0^\infty J^{\nu+1}(uc)\, J^\nu(ua_1)\, J^\nu(ua_2) \ldots J^\nu(ua_n) \frac{du}{u^{\nu(n+1)}} = \frac{1}{[2^\nu\, \Gamma(1+\nu)]^{n-1}},$$

$$W_2 = \frac{c}{a^\nu_1 a^\nu_2 \ldots a^\nu_n} \int_0^\infty J^{\nu+2}(uc) J^\nu(ua_1) J^\nu(ua_2) \ldots J^\nu(ua_n) \frac{du}{u^{\nu(n-1)+1}} = \frac{c^2 - a_1^2 - a_2^2 \ldots - a_n^2}{2[2^\nu\, \Gamma(1+\nu)]^{n-1}}.$$

$$(c > a + a + \ldots + a_n).$$

Still in a second case the values of the integrals W_1 and W_2 are known. Let a_1 exceed all other numbers a and let us put

$$a_1 > c + a_2 + \ldots + a_n.$$

It is necessary then for all values of $\varphi_1, \varphi_2, \ldots, \varphi_{n-1}$ that the closing side of the broken line be greater than c and taking into consideration the two integral-theorems, serving as starting point, we conclude that the integrals W_1 and W_2 have both become zero.

3. We might ask whether results as arrived at above are also attained when the functions $J(ua)$ behind the sign of integration have not all the same parameter. The following operation shows that this is partly the case. Supposing that $\mu_1, \mu_2, \ldots, \mu_n$ are numbers greater than ν, then under a definite condition the evaluation of the integrals

$$W_3 = \frac{c^{\nu+1}}{a_1^{\mu_1} a_2^{\mu_2} \ldots a_n^{\mu_n}} \int_0^\infty J^{\nu+1}(uc)\, J^{\mu_1}(ua_1)\, J^{\mu_2}(ua_2) \ldots J^{\mu_n}(ua_n) \frac{du}{u^{\Sigma\mu-\nu}},$$

$$W_4 = \frac{c^{\nu+2}}{a_1^{\mu_1} a_2^{\mu_2} \ldots a_n^{\mu_n}} \int_0^\infty J^{\nu+2}(uc)\, J^{\mu_1}(ua_1)\, J^{\mu_2}(ua_2) \ldots J^{\mu_n}(ua_n) \frac{du}{u^{\Sigma\mu-\nu+1}}$$

can be reduced to that of the integrals W_1 and W_2.

For the reduction of W_3 and W_4 we can repeatedly apply the formula[1])

$$J^{\mu}(ua) = \frac{(ua)^{\mu-\nu}}{2^{\mu-\nu-1}\,\Gamma(\mu-\nu)} \int_0^{\frac{\pi}{2}} J^{\nu}(ua \cos \alpha) \cos^{\nu+1} \alpha \sin^{2\mu-2\nu-1} \alpha \, d\alpha .$$

We obtain in this way

$$W_3 = \frac{1}{2^{\Sigma\mu-n\nu}} \cdot \frac{2}{\Gamma(\mu_1-\nu)} \int_0^{\frac{\pi}{2}} \cos^{2\nu+1} \alpha_1 \sin^{2\mu_1-2\nu-1} \alpha_1 d\alpha_1 \ldots .$$

$$\ldots . \frac{2}{\Gamma(\mu_n-\nu)} \int_0^{\frac{\pi}{2}} \cos^{2\nu+1} \alpha_n \sin^{2\mu_n-2\nu-1} \alpha_n d\alpha_n \times$$

$$\times \frac{c^{\nu+1}}{(a_1 \cos \alpha_1)^{\nu} \ldots (a_n \cos \alpha_n)^{\nu}} \int_0^\infty J^{\nu+1}(uc)\, J^{\nu}(ua_1 \cos \alpha_1) \ldots J^{\nu}(ua_n \cos \alpha_n) \frac{du}{u^{\nu(n-1)}},$$

$$W_4 = \frac{1}{2^{\Sigma\mu-n\nu}} \cdot \frac{2}{\Gamma(\mu_1-\nu)} \int_0^{\frac{\pi}{2}} \cos^{2\nu+1} \alpha_1 \sin^{2\mu_1-2\nu-1} \alpha_1 d\alpha_1 \ldots .$$

$$\ldots . \frac{2}{\Gamma(\mu_n-\nu)} \int_0^{\frac{\pi}{2}} \cos^{2\nu+1} \alpha_n \sin^{2\mu_n-2\nu-1} \alpha_n d\alpha_n \times$$

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[1]) NIELSEN, page 181.

$$\times \frac{c^{\nu+2}}{(a_1 \cos \alpha_1)^{\nu} \ldots (a_n \cos \alpha_n)^{\nu}} \int_0^{\infty} J^{\nu+2}(uc)\, J^{\nu}(ua_1 \cos \alpha_1) \ldots J^{\nu}(ua_n \cos \alpha_n) \frac{du}{u^{\nu(n-1)+1}}.$$

If now is given $c > a_1 + a_2 + \ldots + a_n$, then during the integration the inequality

$$c > a_1 \cos \alpha_1 + a_2 \cos \alpha_2 + \ldots + a_n \cos \alpha_n$$

will continually hold and the results concerning the integrals W_1 and W_2 can be applied.

Remembering that we have

$$\frac{2}{\Gamma(\mu-\nu)} \int_0^{\frac{\pi}{2}} \cos^{2\nu+1} \alpha \sin^{2\mu-2\nu-1} \alpha d\alpha = \frac{\Gamma(1+\nu)}{\Gamma(1+\mu)},$$

$$\frac{2}{\Gamma(\mu-\nu)} \int_0^{\frac{\pi}{2}} \cos^{2\nu+3} \alpha \sin^{2\mu-2\nu-1} \alpha d\alpha = \frac{\Gamma(2+\nu)}{\Gamma(2+\nu)},$$

we finally find

$$W_3 = \frac{c^{\nu+1}}{a_1^{\mu_1} a_2^{\mu_2} \ldots a_n^{\mu_n}} \int_0^{\infty} J^{\nu+1}(uc)\, J^{\mu_1}(ua_1)\, J^{\mu_2}(ua_2) \ldots J^{\mu_n}(ua_n) \frac{du}{u^{\Sigma\mu-\nu}} =$$

$$= \frac{\Gamma(1+\nu)}{2^{\Sigma\mu-\nu}\, \Gamma(1+\mu_1)\, \Gamma(1+\mu_2) \ldots \Gamma(1+\mu_n)},$$

$$W_4 = \frac{c^{\nu+2}}{a_1^{\mu_1} a_2^{\mu_2} a_n^{\mu_n}} \int_0^{\infty} J^{\nu+2}(uc) J^{\mu_1}(ua_1) J^{\mu_2}(ua_2) \ldots J^{\mu_n}(ua_n) \frac{du}{u^{\Sigma\mu-\nu+1}} =$$

$$= \frac{\left(c^2 - \frac{\nu+1}{\mu_1+1} a_1^2 - \frac{\nu+1}{\mu_2+1} a_2^2 \ldots - \frac{\nu+1}{\mu_n+1} a_n^2\right) \Gamma(1+\nu)}{2^{\Sigma\mu-\nu+1}\, \Gamma(1+\mu_1)\, \Gamma(1+\mu_2) \ldots \Gamma(1+\mu_n)}.$$

$$(c > a_1 + a_2 + \ldots + a_n).$$

In particular we find out of the obtained value for W_3 for $\mu = \frac{1}{2}$, $\nu = -\frac{1}{2}$

$$\int_0^{\infty} \frac{\sin uc \sin ua_1 \sin ua_2 \ldots \sin ua_n}{u^{n+1}} du = \frac{\pi}{2} a_1 a_2 \ldots a_n,$$

for $\mu = -\frac{1}{2}$, $\nu = -\frac{1}{2}$

$$\int_0^{\infty} \frac{\sin uc \cos ua_1 \cos ua_2 \ldots \cos ua_n}{u} du = \frac{\pi}{2}.$$

Mathematics. — "*A family of differential equations of the first order.*" By Prof. JAN DE VRIES.

(Communicated in the meeting of February 27, 1909).

1. The tangent in (x, y) to the integral curve of

$$\frac{dy}{dx} = P(x)\, y + Q(x)$$

is represented by

$$Y - y = \{P(x)\, y + Q(x)\}\,(X - x).$$

For the points of the line $x = m$ we have thus

$$\{\, Q_m (X - m) - Y \,\} + y\, \{\, P_m (X - m) + 1 \,\} = 0.$$

The tangents indicated by them form therefore a pencil of rays having the point

$$x_0 = m - \frac{1}{P_m}\,, \quad y_0 = - \frac{Q_m}{P_m}$$

as vertex.

I call this point the *pole* of the line $x = m$.

By a projective transformation the linear equation is transformed into a differential equation, determining a pencil of rays of which each ray has a definite pole. Each line, connecting the vertex S of that pencil with a pole, having to touch in S an integral curve S is a *singular point*, i. e. a point where y' is indefinite. To confirm this we transform the linear equation by the substitution

$$x = \frac{a_1 u + a_2 v + a_3}{c_1 u + c_2 v + c_3} = \frac{\alpha}{\gamma}\quad, \quad y = \frac{b_1 u + b_2 v + b_3}{c_1 u + c_2 v + c_3} = \frac{\beta}{\gamma}.$$

On account of that

$$y' = P(x)\, y + Q(x)$$

passes into

$$\frac{dv}{du} = \frac{(a_1\gamma - c_1\alpha)\,(\beta P^* + \gamma Q^*) - (b_1\gamma - c_1\beta)\gamma}{(b_2\gamma - c_2\beta)\,\gamma - (a_2\gamma - c_2\alpha)(\beta P^* + \gamma Q^*)}$$

where

$$P^* = P\left(\frac{\alpha}{\gamma}\right), \qquad Q^* = Q\left(\frac{\alpha}{\gamma}\right).$$

The pencil $x = m$ is then transformed into the pencil of rays

$$\alpha = m\gamma.$$

For $\alpha = 0$, $\gamma = 0$ we really find $\dfrac{dv}{du} = \dfrac{0}{0}$. 1)

---

1) Also the points $\beta = 0$, $\gamma = 0$ and $\gamma = 0$, $P^* = 0$ are singular.

A pencil of rays with the indicated property I call *critical.*

From the following ensues the property:

When a singular *point of a differential equation of the first order is the vertex of a* critical pencil of rays, *then this equation can be reduced by a projective transformation into a* linear *one.*

If $x=x_1$, $y=y_1$ is the vertex of a critical pencil, then the substitution

$$x-x_1=\frac{1}{v} \quad , \quad y-y_1=\frac{u}{v}$$

leads to the aim in view.

EXAMPLE I.

The equation

$$\frac{dy}{dx}=\frac{x^3+2x^2y+xy^3+y^4}{x^3+x^2y^2+xy^3}$$

has in $x=0$, $y=0$ a singular point.

The tangent in a point of the line $y=mx$ is indicated by

$$Y-mx=\frac{(m+1)\,m^3x+2m+1}{(m+1)\,m^2x+1}\,(X-x).$$

By reduction it is evident that the parameter x appears here only linear; so the pencil is critical.

For the locus of the poles we find the cubic curve

$$x=-\frac{1}{(m+1)\,m^2}\ ,\ y=-\frac{2m+1}{(m+1)\,m^2}\,.$$

By the substitution

$$x=\frac{1}{v}\ ,\ y=\frac{u}{v}$$

$y=mx$ passes into $u=m$, and the given equation into

$$\frac{dv}{du}+\frac{v}{u+1}+u^2=0\,.$$

2. Let us treat in particular the equation

$$\frac{dy}{dx}=P(x)y\,.$$

Here the locus of the poles of $x=m$ is the line $y=0$ (*polar line*).

As the homogeneous equation

$$\frac{d\eta}{d\xi}=f\left(\frac{\eta}{\xi}\right)$$

has the critical pencil of rays $\eta=m\xi$, with the line at infinity as *polar line*, the question arises whether it is possible to transform the homogeneous equation projectively into an equation of the form $y' = P(x)y$.

If we put

$$\xi = \frac{1}{y} \;,\; \eta = \frac{x}{y} \;,$$

then the right line at infinite distance passes into $y = 0$, the pencil of rays $\eta = m\xi$ into the pencil $x = m$ and the differential equation into the divided equation

$$\frac{dy}{y} = \frac{dx}{x - f(x)} \, .$$

Also the equation

$$\frac{dy}{dx} = Q(x)$$

has for the critical pencil $x = m$ a *polar line*, namely the line at infinity. So here the vertex of the pencil lies on the polar line.

As we can always regulate a projectivity between two point-fields in such a way that a point and a line of the first field are conjugated to a definite point and a definite line of the second, the property holds:

If to a singular *point belongs a* polar line, *the differential equation can be transformed projectively into a divided equation of the form*

$$\frac{dy}{y} = P(x)\, dx,$$

unless the polar line *passes* through *the singular point. In this case we arrive by projective transformation at a divided equation of the form*

$$dy = Q(x)\, dx.$$

EXAMPLE II.

The equation

$$\frac{dy}{dx} = \frac{y^2 - x}{xy + x}$$

has two critical pencils of rays:

$y = mx$ with the polar line $x + y = 0$,

$y + 1 = m(x - 1)$ with the polar line $x = 0$.

For the former pencil the vertex lies on the polar line. By the transformation

$$x = \frac{u}{v} \;\;,\;\; y = \frac{1-u}{v} \;\;,\;\; x + y = \frac{1}{v}$$

this line is thrown to infinity, whilst $y = mx$ passes into $u = 1 : (m + 1)$. We find

$$\frac{dv}{du} = \frac{u-1}{u} \;,\; u - v = lg\, u + C$$

and finally from this

$$\frac{x-1}{x+y} = lg \frac{x}{x+y} + C.$$

To make use of the second pencil we determine a projective transformation, which transforms $(y + 1) : (x - 1)$ into a linear function of u and $x = 0$ into $v = 0$. These conditions are satisfied by the substitution

$$x = \frac{v}{u+v} \;,\; y = \frac{u-v+1}{u+v} \;,\; \frac{y+1}{x-1} = -\frac{2u+1}{u}.$$

We now find

$$\frac{dv}{v} = \frac{u\, du}{(u+1)^2}.$$

3. When the linear equation

$$y' = P(x)y + Q(x)$$

has a *polar line* we can transform this projectively into the line at infinity. The *linear* equation is then transformed into a *homogeneous* one, or, where this is not possible into an equation of the form

$$\frac{dv}{du} = f(u).$$

In the latter case $u = m$ is the critical pencil; in the former where

$$\frac{dv}{du} = f\left(\frac{v}{u}\right)$$

the point $u = 0$, $v = 0$ is the vertex of the critical pencil of rays.

Let

$$ax + by + c = 0$$

be the polar line of

$$y' = P(x)y + Q(x),$$

thus the locus of the pole

$$x = m - \frac{1}{P_m} \;,\; y = -\frac{Q_m}{P_m}.$$

If we put

$$m - \frac{1}{P_m} = f_m \,,$$

then

$$Q_m = \frac{af_m + c}{b(m - f_m)},$$

and the linear equation obtains the form

$$b(x - f(x))\, y' = by + af(x) + c.$$

It is clear, that by the substitution

$$ax + by + c = \frac{1}{u} \quad , \quad x = \frac{v}{u}$$

the polar line is brought to infinity and the point of intersection of the rays $x = m$ is brought into the origin.

After some reduction we find indeed the *homogeneous* equation

$$\frac{dv}{du} = f\left(\frac{v}{u}\right).$$

This reduction is apparently of no use when the polar line has as equation $x + c = 0$. Then

$$m - \frac{1}{P_m} = - c,$$

and the linear equation has this form:

$$y' = \frac{y}{x+c} + Q(x).$$

By the substitution

$$x + c = \frac{1}{u} \quad , \quad y = \frac{v}{u}$$

the polar line is transformed into the line at infinity, the pencil $x = m$ into the pencil $u = 1:(m + c)$, and we find the divided equation

$$dv + Q\left(\frac{1}{u} - c\right)\frac{du}{u} = 0.$$

4. Let us look at a few more examples.

Example III. The equation

$$\frac{dy}{dx} = \frac{xy - y^2 + 2}{x^2 - xy - 2}$$

has singular points in $x = 1$, $y = -1$; $x = -1$, $y = 1$ and in the point at infinity on $x = y$.

The pencil $x - y = m$ is critical. We find for the tangent

$$(my + m^2 - 2)(Y - y) = (my + 2)(X - y - m),$$

and out of this the *polar line* $x + y = 0$.

By the transformation

$$x = v + u \quad , \quad y = v - u$$

the pencil $x - y = m$ passes into the pencil $2u = m$, the polar line into $v = 0$, and we find, as we ought to, the divided equation

$$\frac{dv}{v} = \frac{u\,du}{u^2-1}.$$

Finally we find as integral curves the conics

$$(x-y)^2 + C(x+y)^2 = 4,$$

touching one another in the singular points $x = \pm 1, y = \mp 1$. The point of intersection of the lines $x - y = m$ is the double point of the pair of lines $(x-y)^2 = 4$.

When applying the transformation $x + y = \frac{2}{u}$, $x - y = \frac{2v}{u}$ we find that $x - y = m$ passes into $v = \frac{1}{2} mu$, whilst the polar line is brought at infinity. We find then, as we ought to, a homogeneous equation, namely

$$\frac{dv}{du} = \frac{u}{v}.$$

For a ray of the pencil

$$y + 1 = m(x-1)$$

we find

$$y' = \frac{(x-1)y - (y-2)(y+1)}{(x-1)(x+2) - x(y+1)} = \frac{y - m(y-2)}{x+2-mx} = \frac{(m-1)mx + (1-2m-m^2)}{(m-1)x-2},$$

thus for the tangent

$$[(m-1)x-2]\,Y = [(m-1)mx + (1-2m-m^2)]\,X + 2(m+1).$$

Therefore this pencil is also critical. The poles lie on the line $y - x = 2$.

EXAMPLE IV.

The equation

$$y' = \frac{xy - y^2 + y}{x^2 - xy - y + 1}$$

has $x = 0$, $y = 1$ as singular point.

The pencil $y - 1 = mx$ is critical and has $y = 0$ as polar line. By the substitution $y - 1 = ux$,

$$x = -\frac{1}{u+v} \quad , \quad y = \frac{v}{u+v}$$

we find the divided equation

$$\frac{dv}{v}=\frac{u+1}{u^2+1}\,du.$$

EXAMPLE V.

The equation

$$(x^2-y)\,y'=xy-1$$

has a singular point in $x=1$, $y=1$, which is the vertex of a critical pencil with the polar line $x+y+1=0$.

By the substitution

$$x-1=\frac{3}{v-u-1}\quad,\quad y-1=\frac{3u}{v-u-1}$$

this pencil passes into $u=$ const., whilst the polar line is transformed into $v=0$. We then find

$$\frac{dv}{v}=\frac{u-2}{u^2-u+1}\,du.$$

EXAMPLE VI.

The equation

$$xyy'=x+y^2$$

has the critical pencil $y=mx$ with the polar line $x=0$ passing through the vertex. In connection with this the substitution

$$x=\frac{1}{v}\quad,\quad y=\frac{u}{v}$$

furnishes the divided equation

$$udu+dv=0.$$

The integral curves

$$y^2+2x=Cx^2$$

are conics having in O a contact of four points with $x=0$ as tangent.

EXAMPLE VII. $$x^3\frac{dy}{dx}=x^2y+y^2.$$

This equation of BERNOULLI has a critical pencil $y=mx$ with the polar line $x=0$. By the substitution $x=1:v$, $y=u:v$ it is transformed into $u^{-2}du+dv=0$. Out of this we find $x^2-y+Cxy=0$.

5. When each ray through a singular point determines a system of tangents with *index two*, then the equation is projectively reducible to an equation of the form

$$\frac{dy}{dx}=\frac{N(x)y^2+P(x)y+Q(x)}{R(x)y+S(x)}.$$

For, this equation determines for $x=m$ the tangents of a conic and by the substitution

$$x=\frac{\alpha}{\gamma}\,, \qquad y=\frac{\beta}{\gamma}$$

(see § 1) it is transformed into an equation having in $\alpha=0$, $\gamma=0$ a singular point, whilst each ray of the pencil $\alpha=m\gamma$ possesses the above indicated property.

The equation

$$x\frac{dy}{dx}=\frac{x^3+y^3-2x^2y^2-xy}{y^2-2x^2y-x}$$

is in this case, for each ray $y=mx$ furnishes a system of tangents with index two. By the substitution

$$x=\frac{1}{v}\,, \qquad y=\frac{u}{v}$$

it passes into the equation (of RICCATI)

$$\frac{dv}{du}=2u-u^2v+v^2.$$

This can be reduced with the aid of the solution $v=u^2$ to the equation (of BERNOULLI)

$$\frac{dw}{du}=u^2w+w^2,$$

where $w=v-u^2$. By $w=z^{-1}$ we then arrive at a linear differential equation.

Botany. — Mr. VAN DER STOK presents in behalf of S. H. KOORDERS a communication entitled: "*Polyporandra Junghuhnii, a hitherto undescribed species of the order of Icacinaceae, found in 's Rijks Herbarium at Leiden by* S. H. KOORDERS" *(Plantae Junghuhnianae ineditae II)* [1]).

(Communicated in the meeting of February 27, 1909).

Polyporandra Junghuhnii, KDS *n. spec. Frutex? scandens, ramulis teretiusculis novellis pubescentibus. Folia opposita, oblonga, basi acuta vel obtusa, apice sensim acuminata;* 12—13 *cm. longa et* 4—5 *cm. lata, petiolo* 1—1½ *cm. longo, subcoriacea, supra praeter costam*

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[1]) Continuation of *Plantae Junghuhnianae ineditae I* in Proceedings of the Mathematical and Physical Section, of June 27 1908, p. 158—162.

sulcatam pubescentem glabra, subtus puberula et trinervia, nervis lateralibus utrinque 5—7 adscentibus in margine exeuntibus, nervis secundariis inter primarios transversis atque venis reticulatis, subtus distincte prominentibus. Cirrhi in specimine Jungh. desunt. Flores dioici: masc. nondum aperti, cymoso-paniculati; feminei ignoti. Inflorescentiae axillares laxae folium subaequantes; pedunculi pedicellique pubescentes; bracteae caducissimae (?), in specimine Jungh. deficientes; pedicelli alabastris oblongis breviores; calyx sub-campanulatus 5-*partitus,* 2 *mm. longus, laciniis lanceolatis scariosis, erectis, acuminatis* 1—1.2 *millim. longis, extus appresse pilosis. Petala* 5 *crassiuscula, calyce breviores, extus pilis longis appressis albis. Stamina* 5—6 *rarissime* 7 *filamentis brevissimis, teretiusculis, glabris; antheris oblongis vel linearibus* 8—10-*locularibus. Pollen globoso-tetraëdrum laeve* 10 μ *diam. Ovarium rudimentum subnullum. Fructus ignotus.*

SUMATRA: "*Hochangkola-Tobing*" *(leg.* JUNGHUHN *anno?* 1839. — *Plantae Junghuhnianae ineditae n.* 542 *in Herb. Lugd. Batav.).*

The species described above is the third representative of the genus *Polyporandra* BECC., belonging to the *Icacinaceae* and related to *Jodes* Bl. This species, *Polyporandra Junghuhnii*, was found by me in 1908 in 's Rijks Herbarium at Leiden (*Plantae Junghuhnianae ineditae* N°. 542) and had been collected by JUNGHUHN in the Battak country at "Hochangkola-Tobing". It differs *i. a.* from the two already known species of *Polyporandra* in the structure of the calyx; in *P. scandens* BECCARI (in Malesia I (1877) 125 tab. 7) and *P. Hansemanni* ENGLER (in ENGLER Botan. Jahrb. XVI, Beiblatt, N°. 39 (1893) 13) the calyx is cup-shaped and has short teeth, whereas in *Polyporandra Junghuhnii* it is 5-partite, with pointed segments 1 millim. long.

Superficially the flowers of *Polyporandra Junghuhnii* somewhat resemble these of *Natsiatum herpeticum* BUCHAN, but our *Polyporandra* is sharply differentiated from their species by the characteristic structure of the anthers, described above.

That our species must be included in the above-mentioned genus *Polyporandra* BECC., seems to me to be highly probable. Since however, all the material, which has as yet been found, consists of a single dried branch with young, not completely developed male flowers, floral bud and three leaves, I consider it possible that afterwards, when the as yet unknown female flower, fruits and seeds of *Polyporandra Junghuhnii* shall have been found, this species will prove to be the type of a new sub-genus of *Polyporandra* or of a new genus, directly intermediate between *Polyporandra* BECC. and *Natsiatum* BUCHAN. Because the material is so incomplete, I have, however, thought it advisable to refrain even from proposing a new sub-genus and to assign to this species a place in the genus *Polyporandra*.

In the Herbarium of the Royal Botanic Gardens at Kew I last year compared authentic specimens of the only hitherto described species of *Polyporandra* (*P. scandens* BECCARI and *P. Hansemanni* ENGLER) with JUNGHUHN's unicum of the Leiden Herbarium. In so doing I have become convinced that *Polyporandra scandens* and *Hansemanni* are very closely related but that, as was indicated above, our species (*Polyporandra Junghuhnii*) is sharply marked off from these specifically.

In conclusion I wish to tender my best thanks to the Director of the Royal Botanic Gardens in Kew, for the facilities given me for the comparison of the above-mentioned authentic specimens of BECCARI and of ENGLER.

Leiden, February 26th, 1909.

Physics. — "*On the solid state*". By Mr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ.)

(Communicated in the meeting of February 27, 1909).

1. In a recently published paper [1]) I treated the complete theory of association, not only for gases and vapours, but also for liquids.

If we assume that only two simple molecules combine to a double molecule, the formula:

$$\frac{\beta^2}{1-\beta^2}=\frac{cT^{\gamma+1}\,e^{-\frac{q_0+(p+a/v^2)\Delta b}{RT}}}{p+a/v^2}\quad,\quad .\quad .\quad .\quad .\quad (a)$$

holds universally, in which c is a constant to be determined, and further:

$$\gamma=\frac{-k_1+2k_2}{R}\quad;\quad \Delta b=-b_1+2b_2\,.$$

So the quantity γR is the change of the specific heat for infinitely great constant volume, when 1 Gr. mol. of double molecules passes into 2 Gr. mol. of single molecules, while Δb is the change of the volume of the molecules in this transition. The quantity $q_0=-(e_1)_0+2(e_2)_0$ represents the absorption of heat for $T = 0$ taking place in this transition, and in the first member is β the degree of dissociation of the double molecules.

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[1]) In the *Arch. Teyler* (2) T. **11**, Troisième partie, p. 235—331 (1909).

Besides various other things I demonstrated that the known discrepancies between the experimental critical data and those derived from VAN DER WAALS' equation of state in its usual form can be accounted for by the assumption of an association, which would even be still noticeable at the critical point.

I believe that this opinion was already expressed by VAN DER WAALS some years ago (1906) 1), and elaborated by VAN RIJ in his Thesis for the doctorate (1908); it was, however, demonstrated by me in the paper mentioned, that *quantitative* agreement can be obtained only when Δb is *not* $= 0$. Accordingly this quantity Δb plays an important part in my theory, which I drew up as early as 1902 on the occasion of a paper by the late Prof. BAKHUIS ROOZEBOOM. 2)

But it is not about the above matters, however important, that I intend to speak now. I may be allowed to return to what I said on p. 259 of my paper in the Arch. Teyler (p. 25 of the reprint), namely that the isotherms — if Δb is not $= 0$ — present very "remarkable particularities" in the neighbourhood of $v = b$. (See fig. 1 of the plate).

These particularities now consist in this, that the isotherms, [for Δb positive only below a certain limiting temperature (critical temperature)] after having first risen to comparatively high pressures in the neighbourhood of $v = b$, bend back again as far as in the region of low (even negative) pressures, after which they rapidly ascend again for the second time to the highest pressures. We shall namely see that if e.g. Δb is positive, the degree of dissociation β of the double molecules approaches rapidly to 0 in the neighbourhood of $v = b = b_1 + \beta \Delta b$ in consequence of the relation (α), which causes $v - b$, after having first greatly decreased, to increase again. In consequence of this the pressure will decrease, and it will only increase again when $v - b$ begins to diminish again in the neigbourhood of the value $\beta = 0$. If Δb is negative, β will draw near to the limiting value 1, and we shall evidently see the same course appear in the values of $v - b$ and p.

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1) In an address delivered in the Meeting of this Academy of Jan. 1906, which address has unfortunately never been printed, so that only the fact and the subject of the address are known to me. (Cf. also the Thesis for the Doctorate of Dr. VAN RIJ on "Schijnassociatie etc", p. 3 (1908).

2) "Equilibria of phases in the system acetaldehyde + paraldehyde etc." (These Proc. Vol. XI, p. 283). Compare also VAN DER WAALS: "Some observations etc. These Proc. Vol. XI, p. 808.

It is clear that this may cause a new phase to appear, and that besides equilibrium between the vapour phase and the liquid phase as in the ordinary theory of VAN DER WAALS, under particular circumstances equilibrium may occur between the vapour phase and the third phase, or between the liquid phase and the new phase.

This phase, the molecular volume of which is somewhat less for positive Δb than that of the liquid phase, and for negative Δb somewhat larger, cannot be anything but a *solid phase* (amorphous or crystalline), which distinguishes itself from the liquid one in this, that the degree of dissociation of the double molecules (see § 3) is found in the neighbourhood of 0, so that the molecules are for the greater part in the state of *double molecules*; in the liquid state, however, this degree of dissociation can lie between the values 1 and almost 0, depending on whether we have to deal with so-called non-associating or with strongly associating liquids.

It is self-evident that formation of triple or multiple molecules is not excluded in this, but for the sake of simplicity I shall only work out the theory for partially dissociated double molecules in the following pages. The phenomena will not show any quantitative change by the occurrence of multiple molecules.

2. Before proceeding to a fuller discussion of the above formula (a), we shall first briefly repeat its derivation, and also set forth the influence of pressure and temperature on the equilibrium [1]).

In the condition of equilibrium:

$$-\mu_1 + 2\mu_2 = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which $\mu_1 = \frac{\partial \zeta}{\partial n_1}$ and $\mu_2 = \frac{\partial \zeta}{\partial n_2}$ represent the molecular thermodynamic potentials resp. of the double and of the simple molecules, we must substitute the well-known values for μ_1 and μ_2.

Now:

$$\left.\begin{array}{l} \mu_1 = C_1 - \frac{\partial}{\partial n_1}\left[\Omega - RT\, \Sigma n_1 \,.\, \log \Sigma n_1\right] + RT \log c_1 \\ \\ \mu_2 = C_2 - \frac{\partial}{\partial n_2}\left[\Omega - RT\, \Sigma n_1 \,.\, \log \Sigma n_1\right] + RT \log c_2 \end{array}\right\},$$

in which the functions of the temperature C_1 and C_2 are given by:

$$\left.\begin{array}{l} C_1 = -k_1 T\,(\log T - 1) + \left[(e_1)_0 - T(s_1)_0\right] \\ C_2 = -k_2 T\,(\log T - 1) + \left[(e_2)_0 - T(s_2)_0\right] \end{array}\right\},$$

while

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[1]) Cf. Arch. Teyler, l.c.

$$\Omega = \int p dv - pv\,; \qquad c_1 = \frac{n_1}{\Sigma n_1}\,; \qquad c_2 = \frac{n_2}{\Sigma n_1}\,.$$

Hence substitution in (1) gives:

$$(-C_1 + 2C_2) - \left[-\frac{\partial \Omega'}{\partial n_1} + 2\,\frac{\partial \Omega'}{\partial n_2}\right] + RT\,(-\log c_1 + 2 \log c_2) = 0,$$

when $\Omega' = \Omega - RT\,\Sigma n_1 \,.\, \log \Sigma n_1$.

If β is the degree of dissociation of the double molecules, we have:

$$\frac{\partial \Omega'}{\partial \beta} = \frac{\partial \Omega'}{\partial n_1}\frac{dn_1}{d\beta} + \frac{\partial \Omega'}{\partial n_2}\frac{dn_2}{d\beta} = -\frac{\partial \Omega'}{\partial n_1} + 2\,\frac{\partial \Omega'}{\partial n_2}\,,$$

because $n_1 = 1 - \beta$, $n_2 = 2\beta$, so that we may write:

$$(-C_1 + 2C_2) - \frac{\partial \Omega'}{\partial \beta} + RT \log \frac{c_2^{\,2}}{c_1} = 0\,,$$

or as:

$$c_1 = \frac{1-\beta}{1+\beta}\,; \qquad c_2 = \frac{2\beta}{1+\beta}\,,$$

also:

$$\log \frac{4\beta^2}{1-\beta^2} = \frac{(C_1 - 2C_2) + \dfrac{\partial \Omega'}{\partial \beta}}{RT}\,. \quad . \quad . \quad . \quad . \quad . \quad (a)$$

So we must determine the value of $\dfrac{\partial \Omega'}{\partial \beta}$. From:

$$p = \frac{(1+\beta)\,RT}{v-b} - \frac{a}{v^2}$$

follows:

$$\int p dv = (1+\beta)\,RT \log (v-b) + \frac{a}{v}\,,$$ 1)

so that we find for Ω' $(\Sigma n_1 = 1 + \beta)$:

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1) In this integration the quantity β must namely be kept constant, because an eventual *equilibrium* between the components exerts no influence on the determination of the values of Ω', $\dfrac{\partial \Omega'}{\partial n_1}$ and $\dfrac{\partial \Omega'}{\partial n_2}$ for the two components. In the calculation of the thermodynamical potentials of the different components of an arbitrary mixture we have namely not to take account of a later eventual occurrence of an equilibrium. Thus we calculate here μ_1 and μ_2 quite independently, and simply introduce for the equilibrium the additional condition $-\mu_1 + 2\mu_2 = 0$. So we must imagine the integration $\int p dv$ for a *perfectly arbitrary* ratio of mixing β, which quantity β does not become the degree of dissociation of equilibrium until *after* the introduction of the condition $\mu_1 = 2\mu_2$. (see also Arch. Teyler p. 4).

$$\Omega' = (1+\beta)\, RT \log \frac{v-b}{1+\beta} + \frac{a}{v} - pv\,,$$

hence (a independent of β, see further below):

$$\frac{\partial \Omega'}{\partial \beta} = RT \log \frac{v-b}{1+\beta} - RT + \frac{(1+\beta)\, RT}{v-b}\left(\frac{\partial v}{\partial \beta} - \frac{db}{d\beta}\right) - \frac{a}{v^2}\frac{\partial v}{\partial \beta} - p\frac{\partial v}{\partial \beta}\,.$$

But in consequence of the equation of state all the terms with $\frac{\partial v}{\partial \beta}$ disappear, hence we get:

$$\frac{\partial \Omega'}{\partial \beta} = RT \log \frac{RT}{p + {}^{a}/_{v^2}} - RT - \left(p + \frac{a}{v^2}\right)\Delta b\,, \quad . \quad . \quad . \quad . \quad . \qquad (b)$$

when we represent $\frac{db}{d\beta} = -b_1 + 2b_2$ by Δb. For b we may namely write:

$$b = b_1(1-\beta) + b_2 \,.\, 2\beta = b_1 + \beta(-b_1 + 2b_2) = b_1 + \beta \Delta b.$$

For a may be written:

$$a = (1-\beta)^2 a_1 + 2(1-\beta)\, 2\beta \,.\, a_{12} + 4\beta^2 a_2\,.$$

But in case of simple *association* evidently $a_2 = {}^1/_4\, a_1$, $a_{12} = {}^1/_2\, a_1$, so that:

$$a = (1-\beta)^2 a_1 + 2(1-\beta)\,\beta \,.\, a_1 + \beta^2 a_1 = a_1\,,$$

independent of β.

For the relation (a) we may now write:

$$\log \frac{4\beta^2}{1-\beta^2} = \left[C_1 - 2C_2 + RT \log RT - RT \log\left(p + \frac{a}{v^2}\right) - \right.$$
$$\left. - RT - \left(p + \frac{a}{v^2}\right)\Delta b\right] : RT,$$

or after substitution of the values of C_1 and C_2:

$$\log \frac{\beta^2}{1-\beta^2} = \left[T(\log T - 1)(-k_1 + 2k_2) - (-(e_1)_0 + 2(e_2)_0) + \right.$$
$$+ T(-(s_1)_0 + 2(s_2)_0) + RT \log R + RT \log T - RT - RT \log 4 -$$
$$\left. - RT \log\left(p + \frac{a}{v^2}\right) - \left(p + \frac{a}{v^2}\right)\Delta b\right] : RT.$$

If we now put:

$$\left.\begin{array}{l} -\dfrac{-k_1 + 2k_2}{R} + \dfrac{-(s_1)_0 + 2(s_2)_0}{R} + \log R - 1 - \log 4 = \log c \\[2ex] \dfrac{-k_1 + 2k_2}{R} = \gamma\,; \qquad -(e_1)_0 + 2(e_2)_0 = q_0 \end{array}\right\},$$

we get:

$$\log \frac{\beta^2}{1-\beta^2} = \log c + \gamma \log T - \frac{q_0}{RT} + \log T - \log \left(p + \frac{a}{v^2}\right) - \frac{p+{}^a/_{v^2}}{RT}\,\Delta b\ ,$$

or finally:

$$\frac{\beta^2}{1-\beta^2} = \frac{cT^{\gamma+1}\, e^{-\frac{q_0}{RT}}\, e^{-\frac{p+{}^a/_{v^2}}{RT}\Delta b}}{p + {}^a/_{v^2}}\ , \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

being the most general equation for the binary dissociation in arbitrary state of aggregation. The term with Δb disappears in the gaseous state, for then $\frac{p+{}^a/_{v^2}}{RT} = \frac{1+\beta}{v-b}$, so that then $\frac{\Delta b}{v-b} = \frac{\Delta b}{v}$ verges to 0. But for liquids (and solid bodies), it is by no means allowed to neglect this term (as was nearly always done up to now). For it would be very accidental indeed, if $\Delta b = -b_1 + 2b_2 = 0$. It is just this term with Δb, which exerts a very great influence on the value of β, and is one of the main causes for the occurrence of the solid state.

For perfect gases $p + \frac{a}{v^2}$ may also be replaced by p, and (2) passes into GIBBS's well-known formula for the binary gas dissociation, e.g. of N_2O_4 into $2NO_2$:

$$\frac{\beta^2}{1-\beta^2} = \frac{cT^{\gamma+1}\, e^{-\frac{q_0}{RT}}}{p}.$$

For the further discussion of the equation (2) we refer to the original Paper in the *Arch. Teyler*; we may only be permitted to make the following general remarks.

If we vary the *pressure* at constant temperature, the second member of (2) will approach to ∞ for $p = 0$ ($v = \infty$) in consequence of the denominator p, hence β to 1. So in the perfect gas state everything is in the state of simple molecules.

But for *high* pressures the behaviour will be of two kinds, depending on whether Δb is positive or negative. For Δb *positive*, i.e. when the volume of two simple molecules is greater than of one double molecule, the second member of (2) will evidently approach to 0, when p approaches to ∞. For then this member becomes $= \frac{e^{-\infty}}{\infty} = 0$. The value of β then approaches also to 0, i.e. there is complete association for $p = \infty$. If, however, Δb is *negative*, so that the volume of the double molecules is larger, the limiting value becomes $\frac{e^{+\infty}}{\infty} = \infty$, and then β

approaches again to 1, after having passed through a minimum value at a certain pressure (i.e. a maximum association). In the *Arch. Teyler* (p. 9) I demonstrated that $\frac{\partial \beta}{\partial p}$ changes its sign in this case, when v has become $= 2(b_1 - b_2) = b_1 - \Delta b$. ($\Delta v$ given by formula (8) on p. 8 loc. cit. is namely $= 0$ then).

With regard to the influence of the *temperature* for constant pressure, it is easy to see that for $T = \infty$ as well as for $p = 0$ the dissociation is complete ($\beta = 1$), because $\gamma + 1$ is always positive.

But for lower temperatures the behaviour will again be different, depending on whether $q_0 + \left(p + \frac{a}{b^2}\right)\Delta b$ (v approaches then b, so that a/b^2 may be substituted for a/v^2) is positive or negative. If this quantity is *positive* [where Δb can be as well + as — (q_0 is always positive)], the second member of (2) approaches 0 at $T = 0$, so also β approaches 0 (complete association). But if $q_0 + \left(p + \frac{a}{b^2}\right)\Delta b$ is negative (which is only possible for Δb negative), β becomes again $= 1$ for $T = 0$, so that then a minimum value of the dissociation (maximum association) is passed through. I showed on p. 16 of the *Arch. Teyler* that $\frac{\partial \beta}{\partial T}$ changes its sign, when (see also p. 15 loc. cit.) $q = q_0 + \gamma RT + \left(p + \frac{a}{v^2}\right)\Delta v = 0$. The value of T for this minimum will depend on the pressure.

As for $\beta = 0$, $b = b_1 + \beta \Delta b$ approaches to b_1, while for $\beta = 1$ the limiting value of b will be $2b_2$, we may also say that for $q_0 + \left(p + \frac{a}{b_1^2}\right)\Delta b$ positive β approaches to 0 at $T = 0$, while for $q_0 + \left(p + \frac{a}{4b_2^2}\right)\Delta b$ negative β will approach to 1 at $T = 0$.

For all this compare the figures 1 to 4 on p. 6 and p. 13 loc. cit.

3. Let us now examine the course of an isotherm in a p-v-diagram at a not too high temperature, and that first for the case that Δb is *negative*. Then, as we saw above, the value of β approaches to 1 for $p = \infty$, i.e. b to $2b_2$, the volume of the simple molecules. So this is smaller than b_1.

The said course is (schematically) represented by fig. 1. (See the plate). Besides the usual maximum at B and the minimum at E of the ideal isotherm, according to the original equation of state of

VAN DER WAALS. another maximum at D and a minimum at C have now made their appearance. To A as vapour phase corresponds the coexisting *solid* phase A'. To P' as solid phase the coexisting liquid phase P''. [cf. also the p-T-diagram of fig. 4 (I), where the line SM runs back in consequence of the fact that Δb is negative, which implies that also Δv is negative for the transition solid-liquid ($P\,P''$). By approximation the quantity Δv is namely $=(\beta_l - \beta_s)\,\Delta b$, in which $\beta_{liq.}$ is always $> \beta_{solid}$]. The pressure of coexistence at $P'P''$ will always be much greater than that at $A'A''$, when the temperature is considerably lower than that of the triple point S (see fig. 4). For not too low values of T we may also have a metastable coexistence gas-liquid QQ'' (cf. figs. 1 and 4). If the temperature is very low (as in the following calculation), β will draw near to 1 only for exceedingly high values of v, whereas for all values of v between A and D the value of β is practically $=0$ (association is complete), as will appear from the following calculation. The minimum value of β, which was mentioned in § 2, then lies in the immediate neighbourhood of 0. Only between the points D and E does β increase rapidly from $\beta=(\pm)\,0$ to $\beta=(\pm)\,1$, and this in consequence of the rapid decrease from $v=(\pm)\,b_1$ to $v=(\pm)\,2b_2$. From E to the highest pressures β remains then in the immediate neighbourhood of 1, and becomes exactly $=1$ for $p=\infty$ ($v=2b_2$). It is self-evident that for higher values of T the values of β for P' and P'' will approach each other more.

At the temperature of the triple point S the three transitions AA', QQ'' (metastable), and $P'P''$ will coincide. There is only one pressure of coexistence (three-phase-pressure).

For temperatures above that of S (comp. fig. 2 and fig. 4 (II)) the coexistence QQ'', which was first metastable, has become stable, whereas AA' has now become metastable, just as $P'P''$. (These last transitions, of course, at not too high values of T). Now only a liquid phase coexists with the vapour phase.

For higher temperatures the minimum at C and the maximum at D will draw nearer to each other, and they will finally coincide in an horizontal point of inflection C,D (comp. fig. 3 and fig. 4 (III)). From this moment we have, therefore, the original isotherm of VAN DER WAALS with the simple coexistence gas-liquid.

At last at still higher temperature (the critical temperature in K) also the last maximum (B) and minimum (E) will coincide.

How all this is modified when Δb is *positive*, and so the line SM runs to the right in fig. 4, will be easily seen by the reader. We shall revert to this in a following paper, and mention now only that then (see fig. 1) $v = 2b_2$ lies on the right of $v = b_1$, and accordingly the solid phase not on the right but on the left of the liquid one. Not C and D, but D and E will then coincide in an horizontal point of inflection (critical point solid-liquid).

4. After the above digression we return again to the shape of the isotherm in fig. 1, and we shall carry out a simple computation to prove our statements. For this purpose we shall first modify the principal equations somewhat.

If we put:

$$\frac{p + {}^a/_{v^2}}{RT}(-\Delta b) = \varphi \quad ; \qquad \frac{RT}{q_0} = \theta,$$

we can write equation (2) in the form:

$$\frac{\beta^2}{1-\beta^2} = \frac{cq_0^{\gamma}}{R^{\gamma+1}}(-\Delta b) \,.\, \theta^{\gamma} e^{-1/\theta} \frac{e^{\gamma}}{\varphi},$$

i. e.

$$\underline{\frac{\beta^2}{1-\beta^2} = \lambda\, \theta^{\gamma} e^{-1/\theta} \frac{e^{\gamma}}{\varphi}}, \quad \ldots \ldots \ldots \quad (3)$$

when

$$\frac{c\, q_0^{\gamma}}{R^{\gamma+1}}(-\Delta b) = \lambda$$

is put.

For

$$p = \frac{(1+\beta)\, RT}{v-b} - \frac{a}{v^2}$$

may evidently be written:

$$\underline{p = \frac{RT}{(-\Delta b)}\varphi - \frac{a}{v^2}}, \quad \ldots \ldots \ldots \quad (4)$$

and the value of v can be calculated from:

$$v = b + (v-b) = b + \frac{1+\beta}{\varphi}(-\Delta b),$$

or as $b = b_1 + \beta\,\Delta b$, from:

$$\underline{v = b_1 - \left(\beta - \frac{1+\beta}{\varphi}\right)(-\Delta b)} \,.\, \ldots \ldots \quad (5)$$

So if we successively assume different values of φ for given values of $\lambda, \gamma, b_1, -\Delta b$ and $\theta\,(T)$, we may calculate for each of them the corresponding values of β, v and p.

If we assume:

$c = 2$ (*Gr. Cal.*); $q_0 = 3200$ (*Gr. Cal.*); $b_1 = 1$; $2b_2 = {}^1/_2$; $a = 2700$, so that

$$-\Delta b = -(-b_1 + 2b_2) = {}^1/_2\,,$$

and [with $R = 2$ (Gr. Kal.)]

$$\lambda = \frac{2 \times (3200)^{3/2}}{2^{5/2}} \times {}^1/_2 = (1600)^{3/2} \times {}^1/_2 = 64000 \times {}^1/_2 = 32000$$

becomes; while for T is taken 9° (absolute), yielding:

$$\varphi = \frac{1}{36}\left(p + \frac{a}{v^2}\right)\;; \quad \theta = \frac{9}{1600}\,,$$

the equations (3), (4) and (5) become:

$$\left.\begin{aligned} \frac{\beta^2}{1-\beta^2} &= 32000 \times \left(\frac{9}{1600}\right)^{\frac{3}{2}} e^{-\frac{1600}{9}} \frac{e^\varphi}{\varphi} = \frac{27}{2}\, e^{-\frac{1600}{9}} \frac{e^\varphi}{\varphi} \\ v &= 1 - \frac{1}{2}\left(\beta - \frac{1+\beta}{\varphi}\right) \;; \quad p = 36\varphi - \frac{2700}{v^2} \end{aligned}\right\} \quad . \quad . \quad (6)$$

For $\underline{\varphi = \infty}$ we get evidently:

$$\beta = 1 \quad ; \quad v = 1 - {}^1/_2\,\beta = {}^1/_2\,(= 2b_2) \quad ; \quad p = \infty\,.$$

For $\underline{\varphi = 185}$ we find:

$$log^{10} \frac{\beta^2}{1-\beta^2} = -\,76{,}077 + 0{,}4343\,\varphi - log^{10}\,\varphi \quad . \quad . \quad . \quad (6^a)$$

$$= -\,76{,}077 + 80{,}343 - 2{,}267 = 1{,}999,$$

because:

$$log^{10} \frac{27}{2} - \frac{1600}{9} \times 0{,}43429 = 1{,}130 - 77{,}207 = -\,76{,}077,$$

in consequence of which:

$$\frac{\beta^2}{1-\beta^2} = 99{,}77 \quad ; \quad \beta = 1 - \frac{1}{199{,}54}\,.$$

So between $\varphi = \infty$ and $\varphi = 185$ β is practically $= 1$.

So we find for v:

$$v = 1 - \frac{1}{2}\left(1 - \frac{1}{200} - \frac{2}{185}\right) = 1 - 0{,}492 = 0{,}508,$$

while:

$$p = 6660 - \frac{2700}{(0{,}508)^2} = 6660 - \frac{2700}{0{,}258} = -\,3800,$$

R being expressed in Gr. Cal. ($R = 2$) in the equation of state, also pv and $\frac{a}{v}$ are expressed in caloric units, so that if v, b etc. are given in cM³ (per Gr. mol), the values of pv and $\frac{a}{v}$ in ergs are found by multiplication by $41,74 \times 10^6$. Then p and $\frac{a}{v^2}$ are expressed in dynes per c.M². But as 1 atm. $= 1,01325 \times 10^6$ dynes per cM²., we find the number of atmospheres of p and $\frac{a}{v^2}$ by multiplication of the found values by $\frac{41.73}{1.013} = 41,20$.

The found pressure which will lie in the neighbourhood of the point E in fig. 1, amounts therefore to $-3800 \times 41,20 = -156600$ atm., from which appears how enormous the distance is of the points D and E at such low temperatures. (At higher temperatures both the term $-76,08$ in the equation for β and the factor 36 in the equation for p will become considerably higher).

In a similar way as above we can now calculate for

$\underline{\varphi = 180}$:

$$log^{10} \frac{\beta^2}{1-\beta^2} = -76,076 + 78,173 - 2,255 = -0,160$$

$$\frac{\beta^2}{1-\beta^2} = 0,692 \quad ; \quad \beta = 0,640$$

$$v = 1 - \frac{1}{2}\left(0,640 - \frac{1,640}{180}\right) = 1 - 0,315 = 0,685$$

$$p = 6480 - \frac{2700}{0,469} = 6480 - 5760 = 720.$$

$\underline{\varphi = 170}$:

$$log^{10} \frac{\beta^2}{1-\beta^2} = -76,077 + 73,829 - 2,230 = -4,478$$

$$\frac{\beta^2}{1-\beta^2} = 0.0000331 \quad ; \quad \beta = 0,00575$$

$$v = 1 - \frac{1}{2}\left(0,0058 - \frac{1,0058}{170}\right) = 1 + 0,0001 = 1,0001$$

$$p = 6120 - \frac{2700}{1,0002} = 6120 - 2700 = 3420.$$

$\underline{\varphi = 160}$:

$$log^{10} \frac{\beta^2}{1-\beta^2} = -76,0,7 + 69,486 - 2,204 = -8,795$$

$$\beta = 0$$

$$v = 1 + \frac{1}{320} = 1,003$$

$$p = 5760 - \frac{2700}{1,006} = 5760 - 2680 = 3080.$$

$\underline{\varphi = 100}$:

$$\beta = 0 \quad ; \quad v = 1 + \frac{1}{200} = 1{,}005$$

$$p = 3600 - \frac{2700}{1{,}010} = 3600 - 2670 = 930.$$

$\underline{\varphi = 50}$:

$$\beta = 0 \quad ; \quad v = 1 + \frac{1}{100} = 1{,}01$$

$$p = 1800 - \frac{2700}{1{,}020} = 1800 - 2650 = -\,850.$$

$\underline{\varphi = 10}$:

$$\beta = 0 \quad ; \quad v = 1 + \frac{1}{20} = 1{,}05$$

$$p = 360 - \frac{2700}{1{,}103} = 360 - 2450 = -\,2090.$$

$\underline{\varphi = 1}$:

$$\beta = 0 \quad ; \quad v = 1 + \frac{1}{2} = 1{,}5$$

$$p = 36 - \frac{2700}{2{,}25} = 36 - 1200 = -\,1160$$

$\underline{\varphi = 0{,}1}$:

$$\beta = 0 \quad ; \quad v = 1 + \frac{1}{0{,}2} = 6$$

$$p = 3{,}6 - \frac{2700}{36} = 3{,}6 - 75 = -\,71.$$

$\underline{\varphi = 0{,}01}$:

$$\beta = 0 \quad ; \quad v = 1 + \frac{1}{0{,}02} = 51$$

$$p = 0{,}36 - \frac{2700}{2601} = 0{,}36 - 1{,}04 = -\,0{,}68.$$

$\underline{\varphi = 0{,}001}$:

$$\beta = 0 \quad ; \quad v = 1 + \frac{1}{0{,}002} = 501$$

$$p = 0{,}036 - \frac{2700}{251000} = 0{,}036 - 0{,}011 = 0{,}025.$$

$\underline{\varphi = 10^{-74}}$:

$$\log \frac{\beta^2}{1-\beta^3} = -\,76{,}077 + 0 + 74 = -\,2{,}077$$

$$\frac{\beta^2}{1-\beta^3} = 0{,}00838 \quad ; \quad \beta = 0.0911$$

$$v = 0{,}546 \times 10^{74} \quad ; \quad p = 36 \quad 10^{-74}.$$

$\varphi = 0$:

$$\beta = 1 \quad ; \quad v = \infty \quad ; \quad p = 0.$$

With regard to the course of the values of we see clearly from this calculation, that between the points $F\,(p = \infty)$ and $E\,(p = -4130)$ in fig. 1 β is practically $= 1$ ($\beta = 0{,}983$ in E). This is due to the fact that between $\varphi = \infty$ and $\varphi = 185$, $log^{10} \dfrac{\beta^2}{1-\beta^2}$ in (6^a) has a comparatively high *positive* value (at $\varphi = 185$ still $= 2$), in consequence of the value of $0{,}4343\,\varphi$, which is then $> -76{,}08$ (this value holds for $T = 9$), so that $\dfrac{\beta^2}{1-\beta^2}$ is large, and β will lie in the neighbourhood of 1 (for $\varphi = 185$ β is still as great as $= 0{,}995$).

But between E and D, i. e. between $\varphi = 185$ and $\varphi = 170$, a *very rapid change* in the value of β takes place. The value of $0{,}4343\,\varphi$ becomes then namely $< -76{,}08$, in consequence of which $log^{10} \dfrac{\beta^2}{1-\beta^2}$ decreases from a positive value to a comparatively large *negative* one (for $\varphi = 170$ already $= -4{,}5$), so that β changes rapidly from 1 to 0. In the point D we have $\beta = 0{,}027$, while $\beta = 0{,}006$ for $\varphi = 170$. For $\varphi = 180$ at about $^2/_3$ of the distance between E and D, we have the intermediate value 0,64.

So the entire change of β takes practically place between the points E and D. Past D β remains practically $= 0$, till at about $\varphi = 10^{-74}$, at an enormous value of v ($v = 0{,}55 \times 10^{74}$), the value of β gradually rises from 0 to 1. In equation (6^a) the term $-log^{10}\varphi$ begins then to approach the term $-76{,}08$ in absolute value, and it exceeds this term for values of $\varphi < 10^{-76}$. For $\varphi = 10^{-74}$ β is already 0,09, while for $\varphi = 0$ ($v = \infty$) β will have become $= 1$. So this transition takes place beyond the limits of the diagram (fig. 1) (for $T = 9$).

What was said above, gives a clear idea of the course of the values of β, and we see at the same time from it, that in the transition solid-liquid ($P'P''$) the value of β_{liquid} is practically $= 1$, and that of β_{solid} practically $= 0$. For the point P'' lies between E and D, and the point P' beyond D.

The corresponding values of p have been indicated everywhere in the figure, while those of v appear from the above calculation.

5. In connection with what was discussed before, we will finally give the calculation of the different maxima and minima in fig. 1, viz. of the points B, C, D and E.

From the equation of state:

$$p=\frac{(1+\beta)RT}{v-b}-\frac{a}{v^2}$$

it is easy to derive for T constant (keeping in mind that $b=b_1+$ $+\beta\,\Delta b$): [1])

$$\frac{dp}{dv}=-\frac{(1-\beta)RT}{(v-b)^2}\left(1 \quad \Delta b\frac{\partial\beta}{\partial v}\right)+\frac{RT}{v-b}\frac{\partial\beta}{\partial v}+\frac{2a}{v^3},$$

i. e. with
$$\frac{(1+\beta)(-\Delta b)}{v-b}=\varphi:$$

$$\frac{dp}{dv}=\frac{2a}{v^3}-\frac{(1+\beta)RT}{(v-b)^2}\left[1-(1-\varphi)\frac{v-b}{1+\beta}\frac{\partial\beta}{dv}\right].$$

But from the equation (2) for β, viz. in the form (written $\frac{(1+\beta)RT}{v-b}$ for $p+\frac{a}{v^2}$):

$$\frac{\beta^2}{1-\beta^2}=\frac{f(T)}{RT}\frac{v-b}{1+\beta}e^{-\frac{(1+\beta)\Delta b}{v-b}},$$

from which p has been eliminated, follows by logarithmical differentiation (T constant) after some reductions (see p. 36—37 loc.cit.):

$$\frac{v-b}{1+\beta}\frac{\partial\beta}{\partial v}=\frac{{}^1/_2\,\beta(1-\beta)(1-\varphi)}{1+{}^1/_2\,\beta(1-\beta)(1-\varphi)^2}.$$

By substitution in the expression for $\frac{dp}{dv}$ obtained above we get now:

$$\frac{dp}{dv}=\frac{2a}{v^3}-\frac{(1+\beta)RT}{(v-b)^2}\,\frac{1}{1+{}^1/_2\,\beta(1-\beta)(1-\varphi)^2}\quad\ldots\quad(7)$$

This expression passes into the ordinary one for $\beta=0$ and 1. [It is true that for $\beta=1$ we obtain $\frac{dp}{dv}=\frac{2a}{v^3}-\frac{2RT}{(v-b)^2}$, but a, v and b referring to double-molecular quantities, $a=4a'$, $v=2v'$, $b=2b'$ will have to be substituted, in which the accentuated quantities now refer to single molecular quantities. We get then $\frac{dp}{dv'}=\frac{2a'}{v'^3}-\frac{RT}{(v'-b')^2}$, as we should get.]

Let us now first examine the points D and E (fig. 1). There $v-b$ is small, so φ large. In this we notice that the just introduced quantity φ is the same as our former quantity φ. For in (3) etc. $\frac{p+a/v^2}{RT}(-\Delta b)=\varphi$ was put, so also $\frac{(1+\beta)(-\Delta b)}{v-b}=\varphi$. Now $\varphi=185$

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[1]) See also Arch. Teyler, l.c. p. 26—27.

for E and $\varphi = 170$ for D (see § 4), so that we may write $^1/_2\,\beta(1-\beta)\,\varphi^2$ instead of $1 + {^1/_2}\,\beta\,(1-\beta)\,(1-\varphi)^2$ — if namely the value of β and $1-\beta$ is not too small. It will presently appear that this is not the case.

So in the points D and E we have got by approximation:

$$\frac{2a}{v^3} = \frac{(1+\beta)\,RT}{(v-b)^2}\;\frac{1}{{^1/_2}\,\beta\,(1-\beta)\dfrac{(1+\beta)^2\,(-\Delta b)^2}{(v-b)^2}} = \frac{RT}{{^1/_2}\,\beta\,(1-\beta^2)\,(-\Delta b)^2}\,.$$

Now in D (see fig. 1) v is in the neighbourhood of b_1, whereas in E the volume v is in the neighbourhood of $2b_2$; hence if we put $1-\beta$ and $1+\beta = 1$ for D, where β is near 0; and $\beta = 1$, $1+\beta = 2$ for E, where β is near 1, we get by approximation ($R = 2$)

$$\beta_D = \frac{2T}{\dfrac{a}{b_1^{\,3}}\,(-\Delta b)^2} \quad ; \quad 1-\beta_E = \frac{T}{\dfrac{a}{(2b_2)^3}\,(-\Delta b)^2}\,.$$

So with $T = 9$, $a = 2700$, $b_1 = 1$, $2b_2 = {^1/_2}$, $-\Delta b = {^1/_2}$ we find:

$$\beta_D = \frac{18}{2700 \times {^1/_4}} = \frac{2}{75} = 0{,}027 \;\; ; \;\; 1-\beta_E = \frac{9}{2700 \times 8 \times {^1/_4}} = \frac{1}{600} = 0{,}0017.$$

So above at D we have neglected 1 by the side of circa $0{,}0133 \times 170^2 = 400$, and at E we have neglected 1 by the side of circa $0{,}00083 \times 185^2 = 28{,}5$; so that the above values of β_D and $1-\beta_E$ may be considered as permissible approximations.

It is now easy to calculate the pressure in the points D and E from the equation of state. With $\dfrac{(1+\beta)\,(-\Delta b)}{v-b} = \varphi$ the latter becomes (see equation (4) and (6)):

$$p = \frac{RT}{-\Delta b}\,\varphi - \frac{a}{v^2} = 36\,\varphi - \frac{2700}{v^2}\,.$$

Hence we find:

$$p_E = 6700 - 10530 = -\,3830,$$

as according to (6^a) $\varphi = 186$ and $v = 0{,}506$ corresponds to $\beta_E = 1 - \dfrac{1}{600}$.

And as $\varphi = 173$ and $v_D = 0{,}99$ corresponds to $\beta_D = 0{,}027$:

$$p_D = 6230 - 2750 = 3480.$$

As to the points B and C, for them $\beta = 0$ for $T = 9$, as we saw before. So there is simply:

$$\frac{2a}{v^3} = \frac{RT}{(v-b)^2}\,,$$

i.e. with $b = b_1 = 1$:

$$\frac{v^3}{(v-1)^2} = 300\,,$$

yielding $v_B = 298$ and $v_C = 1{,}063$.

Hence from:

$$p = \frac{18}{v-1} - \frac{2700}{v^2}$$

we find:

$$p_B = 0{,}0606 - 0{,}0304 = 0{,}0302$$
$$p_C = 280 - 2400 = -2120.$$

So reviewing what has been said, we can account for the appearance of the different maxima and minima in the following way. In the expression $p = \frac{RT}{v-b} - \frac{a}{v^2}$ the term $\frac{RT}{v-b}$ will increase more rapidly than $\frac{a}{v^2}$ between the points A and B, in consequence of the decrease of v, so that p becomes larger. Between B and C, on the other hand, the increase of $\frac{a}{v^2}$ will predominate, so that p decreases. But beyond C, when v comes near b, $\frac{RT}{v-b}$ will again increase more than $\frac{a}{v^2}$, and the isotherm will now ascend very rapidly. It would proceed to $p = \infty$ (according to the original theory), but *in consequence of the abrupt change of the value of* β *between* D *and* E *from* 0 *into* 1, the value of a/v^2 will increase rapidly from a/b^2 to $a/4b_2^2$. For E, where this increase of β has ceased, $v - b$ will begin to decrease again from this moment, so that p can ascend indefinitely.

Hence, when only the *state of association* β of the molecules for small volumes is taken into consideration, in connection with the *variation of volume* Δb attending it, not only the liquid state, but also the *solid state* (crystallized or not) is quite controlled by VAN DER WAALS' equation of state.

Further particulars, referring to the case Δb positive, to the formation of multiple complexes, to different modifications of the solid state, to the ratio $\frac{T_0}{T_c}$, where T_0 is the triple-point temperature, and T_c the ordinary critical temperature, etc. etc., will be discussed in a subsequent paper.

Physics. — *"On the calculation of the pressure of a gas by the aid of the assumption of a canonical ensemble."* By Dr. O. Postma. (Communicated by Prof. H. A. Lorentz.)

(Communicated in the meeting of February 27, 1909).

To the different existing methods for the derivation of the pressure of a gas (or the equation of the isotherm), Gibbs has of late added another, namely the method by the aid of the theory of a canonical ensemble. According to this method we take for the force exerted by a system on an external body in the direction of one of the coordinates a of that body, the value $-\overline{\frac{\partial\varepsilon}{\partial a}}$, the mean of $-\frac{\partial\varepsilon}{\partial a}$ taken over a canonical ensemble. Dr. Ornstein was the first to apply this method [1]). He shows that

$$\overline{A} = -\overline{\frac{\partial\varepsilon}{\partial a}} = -\int e^{\frac{\psi-\varepsilon}{T}} \frac{\partial\varepsilon}{\partial a} d\lambda = -\frac{\partial\psi}{\partial a},$$

in which ψ is determined by $e^{-\frac{\psi}{T}} = \int e^{-\frac{\varepsilon}{T}} d\lambda$. Suppose the gas to be in a cylinder, closed by a piston at a height a, A represents the pressure exercised on this piston. The pressure pro cM². will be represented by $p = -\frac{\partial\psi}{dV}$ and by means of this formula Dr. Ornstein arrives at the known result. If, however, we examine the method somewhat more closely, we are confronted with different difficulties. In the first place it should be borne in mind, that if $A = -\frac{\partial\varepsilon}{\partial a}$ is to denote the force exerted on the piston, the coordinates of the molecules must be thought to be constant in this differentiation [2]). Apart from the energy of gravity, the ε consists of four parts: $\varepsilon_1 =$ the potential energy of the repulsive forces acting between the walls of the vessel and the molecules, $\varepsilon_2 =$ the potential energy of the repulsive forces between the molecules inter se, $\varepsilon_3 =$ the potential energy of the attractive forces, $\varepsilon_4 =$ the kinetic energy. Only the first is a function of a, and it determines the A, which is really $-\frac{\partial \varepsilon_1}{\partial a}$, but which is now also represented by $\frac{\partial \varepsilon}{\partial a}$. Now we notice that the energy of the repulsive forces is taken into account in the calculation of ψ by simply excluding that part of the extension where the molecules would have penetrated into the wall of the vessel or into each other. We may also say ε_1 and ε_2 are put $= 0$ when the molecules do not yet touch the walls, and if they do, put as ∞.

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[1]) Cf "Toepassing der Statistische Mechanica van Gibbs op molekulair-theoretische vraagstukken". Leiden 1908. Further: "Calculation of the pressure of a mixture of two gases by means of Gibbs' statistical mechanics," These Proc. Vol. XVII, p. 116, and "Statistical theory of capillarity", These Proc. Vol. XVII, p. 526.

[2]) When we substitute at once V for a, there is some danger to overlook this.

So the ε_1 and ε_2 have a discontinuous course, and yet it is just on the assumption that a certain extension exists with finite $\frac{\partial \varepsilon_1}{\partial a}$, with respect to which it is integrated after multiplication by the density $e^{\frac{\psi-\varepsilon}{T}}$, that the method is based. So it is certainly desirable to question the validity of this method of calculation. Disregarding the repulsive and attractive forces between the molecules inter se, we have to calculate:

$$\overline{A} = -\int e^{\frac{\psi-\varepsilon}{T}} \frac{\partial \varepsilon_1}{\partial a} d\lambda = -Ce^{\frac{\psi}{T}} \int e^{-\frac{\varepsilon_1}{T}} \frac{\partial \varepsilon_1}{\partial a} dx_1 \ldots dz_n$$

when we have integrated with respect to the velocities. So also:

$$\overline{A} = CTe^{\frac{\psi}{T}} \frac{\partial}{\partial a} \int e^{-\frac{\varepsilon_1}{T}} dx_1 \ldots dz_n.$$

Is it now allowed to take for this integral $\int dx_1 \ldots dz_n$ integrated with respect to the extension limited by the walls of the vessel? Let us consider the simplest conceivable case of an ensemble of one molecule with coordinate of height x. In fig. 1 $e^{-\frac{\varepsilon_1}{T}}$ is given as $f(x)$. AC indicates the distance at which the molecule still repulses the wall. When now the piston is moved over a distance Δa, the line AB moves to $A'B'$ (with or without change of form). The limit of $\frac{\text{area } AB\,B'A'}{\Delta a}$ now represents $\frac{\partial}{\partial a}\int e^{-\frac{\varepsilon_1}{T}} dx$. In fig. 2 the distance AC is reduced to 0, so that $\varepsilon_1 = \infty$ if $x > a$, and $\varepsilon_1 = 0$ and $e^{-\frac{\varepsilon_1}{T}} = 1$ if $x < a$. The figure $ABB'A'$ now becomes a rectangle, which therefore also represents Δ extension with basis Δa. When the area of these two figures becomes equal with decreasing Δa, we may take $\frac{\partial}{\partial a}\int dx = \frac{\partial}{\partial a}\int e^{-\frac{\varepsilon_1}{T}}$ (then both $= 1$). This is the case when in fig. 1

AB is moved parallel to itself, and it is easy to see that this will not be the case if simply $\varepsilon_1 = f(x, a)$, but it will if $\varepsilon_1 = f(a - x)$. This may be assumed here, so the reduction is permissible.

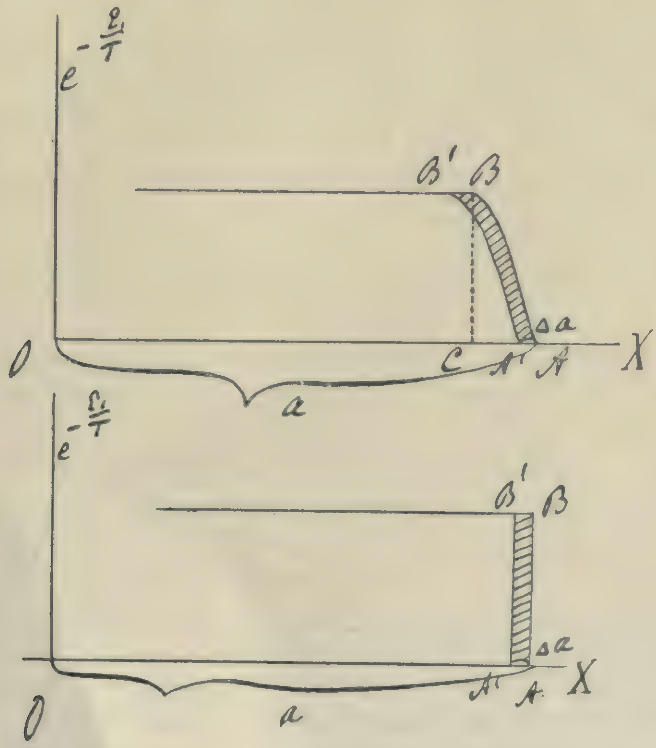
When there are more molecules the reasoning continues to be valid if $\varepsilon_1 = f(a - x_1, a - x_2$ etc.), at least for so far as only the piston is considered.

We meet with a second difficulty, if we take also ε_2 and ε_3 into account; now we may put:

$$A = -\int e^{\frac{\psi-\varepsilon}{T}} \frac{\delta\varepsilon_1}{\delta a}\, d\lambda = -C e^{\frac{\psi}{T}} \int e^{\frac{-\varepsilon_1-\varepsilon_2-\varepsilon_3}{T}} \frac{\delta\varepsilon_1}{\delta a}\, dx_1 \ldots dz_n =$$

$$= -C e^{\frac{\psi}{T}} \int e^{\frac{-\varepsilon_1-\varepsilon_2-\varepsilon_3}{T}} \frac{\delta(\varepsilon_1+\varepsilon_2+\varepsilon_3)}{\delta a}\, dx_1 \ldots dz_n = CTc^{\frac{\psi}{T}} \frac{\delta}{\delta a} \int e^{-\frac{\varepsilon_1+\varepsilon_2+\varepsilon_3}{T}}\, dx_1 \ldots dz_n.$$

Now we may take account of ε_1 and ε_2 by regulating the limits in accordance with them in the way discussed, and further by putting ε_1 and $\varepsilon_2 = 0$ within these limits, while $C - \frac{a}{V}$ may be put for ε_3. It seems, however, to me, that this method comes to this that for ε_2 and ε_3 not $f(x_1 \ldots z_n)$ is taken, as should have been done,


$e^{-\frac{\varepsilon_1}{T}}$
B'
B
Δa
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C
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$e^{-\frac{\varepsilon_1}{T}}$
B'
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Δa
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X
a

but $f(V)$ or $f(a)$, as instead of all possibilities only the most probable distribution is considered. When, however, ε_2 and ε_3 are $f(a)$, the above reduction is not allowed, since there $\frac{\partial \varepsilon_1}{\partial a} = \frac{\partial (\varepsilon_1 + \varepsilon_2 + \varepsilon_3)}{\partial a}$ has been put.

So it seems to me that two errors have been made in this reduction, which have yet made it possible for us to arrive finally at the correct result. First of all ε_2 and ε_3 have been taken constant over the ensemble, which would have the result that $\overline{A}$ would be the same as if ε_2 and ε_3 did not exist, because $A = -\frac{\partial \varepsilon_1}{\partial a}$ is independent of ε_2 and ε_3 for a certain phase. It is just in consequence of the change in phase-distribution which they cause, that ε_2 and ε_3 have influence. In the second place $e^{-\frac{\varepsilon_2}{T}}$ and $e^{-\frac{\varepsilon_3}{T}}$ should now have been put as constant factors before the sign $\frac{\partial}{\partial a}$, in consequence of which we should, in fact, have again obtained the same value as without ε_2 and ε_3. At all events I think I may be justified in calling in question the strictness with which the method has been applied up to now.

Physiology. — *"Contributions to the study of serum-anaphylaxis."* By Dr. J. G. SLEESWIJK, Foreign Member of the PASTEUR Institute at Brussels. (2nd Communication). (Communicated by Prof. C. H. H. SPRONCK).

(Communicated in the meeting of February 27, 1909).

To experimentally bring about the phenomenon of serum-anaphylaxis (RICHET) — which with other related forms of changed power of reaction of the organism is denoted by the general name of Allergy (v. PIRQUET) — consequently at least two serum-injections are necessary. For the first, the sensitizing injection, spores of serum are sufficient, whilst, however, at the end of the incubation-stage a larger dose is wanted to bring about intoxication (which, however, is different again, according as the injection is given intraperitoneally resp. subcutaneously, or into the circulation resp. into the brain).

It has of course been asked, whether these two functions, the sensitization and the intoxication, have to be attributed to the same material or to two different constituents of the serum. Now without entering into the detailed theoretical considerations put up with reference to this, I only wish to point out that in more than one way serum can be deprived of its toxicity for sensitized animals, without at the same time losing its sensitizing power. This also holds good especially for the fluids described in my last communication: serum treated with washed guineapig-blood and the filtrate of dialysed serum, which have both lost their toxicity for sensitized guinea pigs, are nevertheless able to render normal animals sensible to a later injection of horse-serum.

The same is the case with the new method, to be described here after, to deprive the horseserum of his toxicity with the aid of bariumsulphate. Therefore this may be laid down as a general rule. A priori there is no doubt something to be said for the opinion that the sensitizing and the intoxicating principle of horse-serum are represented by two different substances, which apparently may be dissociated with the help of divers biological and physico-chemical processes. I myself, however, should for the present prefer to take an other standpoint, and that for the following reason: taking for granted the fact that for the sensitizing action only traces of serum are required, we may safely assume that in the different methods of destroying the toxic serum principle so much of the active matter is destroyed or fixed, that intoxication can no longer be brought about, but that there is a sufficient quantity left to cause sensibility. Because (and here we have a parallel): for not a single immunebody, whose function can be made to disappear from the serum by heat, there exists a limit for which holds good that after a certain time and for a definite temperature the substance should be altogether destroyed. Even though we can no more prove the presence of such a material by a reaction in vitro, yet the curve, of which the ordinate represents the time and the abscis the temperature, theoretically never reaches zero. And such theoretical possibilities ought to be taken into consideration (as moreover experience has shown in heating horse-serum), when — as appears from serum-sensitization — we can cause a biological reaction with such extremely small quantities of a substance. Therefore I do not see why we should in this respect depart from our generally accepted opinions and why we should not identify the sensitizing antigen with the toxical, if only we bear in mind that the organism reacts upon small doses otherwise than upon large doses. But in this communication we do not want to enter into a more detailed description of the theoretical part of the problem and we will now revert to the facts.

The serum rendered atoxic in one of the above mentioned ways has now, besides its sensitizing power, retained another quality: it has remained vaccinating, i. e. that sensitized guinea-pigs, treated with it, are already within a few hours immune against an otherwise mortally large dose of horse-serum not treated beforehand. Also fresh serum itself, in the usual toxical dose (4—5 cM^3) has vaccinating action, but this is a two-edged sword, because in the majority of cases the animals are killed thereby. Besredka, 1) however, was able to prove, that already with a very small dose of serum (e. g. 0.05 cM^3), injected into the abdomen, a sensitized animal could be vaccinated without showing symptoms of disease. Now this fact — it seems to me — may be said to be on a par with the vaccinating action that I found of larger doses of serum rendered atoxical, and at the same time it suggests the following explanation: for the dissensitizing (vaccinating) of an animal rendered sensitized a definite, very small quantity is wanted of a substance found in fresh horse-serum. The latter, administered at once and in larger quantity, acts moreover toxically (sudden dissensitization, shock); a small dose of serum, however, (Besredka), or — as we have seen — a larger quantity of serum from which the greater part of this substance has been eliminated, contain still enough of it to dissensitize gradually and without toxical by-actions. In passing it may be remarked here that for a probable practical application in the re-injection of therapeutic sera only such a method is practicable, in which is obtained an atoxical and dissensitizing serum, which at the same time has retained a sufficient quantity of antitoxine-units

Further I have asked myself whether it would be possible, in a simple way to get a closer determination of the generally chemical nature of the antigen of anaphylaxis (by this I mean the toxical and vaccinating matter which I consider identical with the sensitizing principle). Does this material belong to the proteins or to the lipoids?

I have tried to answer this question by means of a method which by Bordet and the present writer in a still unfinished investigation about the causes of specificity is applied in the splitting of antigens into a soluble part and another part insoluble in absolute methyl-alcohol free from aceton. Now we take 5 cM^3 of horse-serum (consequently a toxical dose for sensitized guinea pigs), it is dried, rubbed into powder and repeatedly extracted with methyl-alcohol. The alcoholic extract is then, by its being taken up again into a small quantity of alcohol — in which the salts do not dissolve — almost

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1) C. R. Soc. de Biol. 23 Jan. 1909.

entirely freed from it. Both the extract and the residue are now, each in their turn, treated with 5 cM³ of physiological salt-solution and thus reduced to the original volume. The extract yields an homogeneous fatty emulsion; the residue with the water forms into a thick liquid, jelly-like mass[1]). Now the first is quite indifferent to sensible guinea pigs; not only is it absolutely unpoisonous, but the animals remain also after the injection of it as sensible to an injection of fresh serum as before. Meantime the part of the serum not soluble in alcohol, wholly injected into sensitized animals, does not give, or hardly gives, rise to symptoms of poisoning, but vaccinates against a later, in itself toxical, injection with normal serum. For this vaccination, however, very small doses of the residue, as BESREDKA found them sufficient for intact serum, do not suffice Therefore the active part of the serum has, through the action of the alcohol, lost together with its toxicity also a part of its vaccinating power. At any rate the proteine-nature of the antigen of anaphylaxis seems in my opinion to be well proved by what is said above.

In continuation of the methods explained in my former communication to eliminate the toxical principle of horse-serum for sensitized guinea pigs (fixation upon pig-blood, dialysis), I am now able to add to them a third process. It is based upon recent and very important investigations of GENGOU[2]). The latter proved among others, that, while water possesses no capacity of suspension for bariumsulphate, in consequence of which this powder rapidly subsides, this sedimentation changes into a dissemination in the presence of some stable colloids. This dissemination is based upon a molecular adhesion, a real adsorption of the colloid by the powder. To the colloidal solutions that show this quality, belongs among others the serum. From an oral communication of GENGOU which has not yet been published it further appeared to me that this investigator had succeeded, by contact of fresh serum with $BaSO_4$ in salt-solution, in depriving this serum of its alexine. This led me to try if perhaps also the toxical principle of horse-serum would be absorbed by this powder. It really appeared to be the case. For this purpose is used a suspension of bariumsulphate in physiological salt-solution containing about 70 m.gr. $BaSO_4$ per 1 cM³. Three parts of this (or the sediment of it) are treated with 1 part of serum. If, however, instead of physiological salt-solution, distilled water is taken as vehicle for bariumsulphate — or the dry powder, when there is no salt-solution — then the serum remains toxical. The presence of NaCl-solution is therefore necessary, though a very small quantity (some tenths of 1 cM^3 to the 5cM^3 serum) appears to be sufficient. Some titrations of diphtheria-serum treated thus, taught me already that the quantity of antitoxines decreases thereby only to a very low percentage. (Conversely, barium-sulphate, which as a dry powder leaves the anaphylactic powder intact, is able, in this same form, to fix the antitoxines). So where the serum-principle, toxic to hypersensible individuals, and the antitoxical power of antidiptheria-serum can be dissociated according to this process, it seems to me that a priori a practical application thereof is not impossible. It is a purely technical problem to work out these data more closely.

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[1]) Neither is able to fix alexine in vitro, in the presence of anaphylactic pig serum.

[2]) "Contribution à l'étude de l'adhésion moléculaire et de son intervention dans divers phénomènes biologiques." Arch. internat. de Physiol. 1908, Vol. VII.

About the reactions of immunity, which are enacted in the hypersensible organism, I hope to be able to give further information on a following occasion.

Mathematics. — "*Continuous one-one transformations of surfaces in themselves.*" By Mr. L. E. J. Brouwer. (Communicated Prof. D. J. Korteweg).

(Communicated in the meeting of February 27, 1909).

We shall treat in this paper an arbitrary surface, which in the sense of analysis situs is equivalent to a sphere, i. o. w. which is a continuous one-one image of a sphere. We shall submit that surface to an entirely arbitrary continuous one-one transformation in itself and we shall investigate whether this is possible without at least one point remaining in its place.

To simplify we shall consider a continuous one-one image of the surface in a Cartesian plane; the infinity of it then of course forms an exception, because there the continuity of the correspondence is disturbed, and because it must answer as a whole to a single point; for that point we choose a point not remaining invariant in the transformation.

In the Cartesian plane we indicate the points of the untransformed figure by letters without a dash, the corresponding point of the transformed figure by equal letters with a dash. In particular we shall indicate infinity by H and K'.

We now construct in the untransformed figure the system of the circles around K as their centre. These closed curves k lie outside each other, expand from K to H and to each of those curves there is *uniform convergence* [1]) by the preceding ones as well as by the succeeding ones.

In the transformed figure to this answers a system of *single closed curves* [2]) k', which, lying inside each other, contract from K' to H', whilst there is again uniform convergence to each of the curves k' by the preceding ones as well as by the succeeding ones.

Let us now regard, starting from K and stopping in H, each curve k_α together with the corresponding curve k'_α; here α represents the radius of the circle k_α.

We shall assume that the transformation in the surface leaves the indicatrix invariant; then in k and k' opposite senses of circuit correspond to each other.

For values of α under a certain limit α_1 the curve k lies inside k'; beyond a certain value α_r however the curve k' lies continually inside k. Between α_1 and α_r there can be values for which the inner domains of k and k' lie entirely outside each other; these then have an upper limit α_2, situated between α_1 and α_r.

Between a certain nethermost limit α_0 (which with α_2 existing coincides with α_2, otherwise with α_1) and an upper limit α_r, the curves k and k' must continually penetrate each other.

If α_0 and α_r coincide, k_{α_0} and k'_{α_0} do so too, and, opposite senses of circuit corresponding for the transformation on this curve, we find *two points invariant for the transformation.*

We now assume that α_0 and α_r do not coincide. Then k_{α_0} and k'_{α_0} touch each other in one or more points or arcs, without penetrating each other, whilst for the rest they lie either outside each other, or k_{α_0} lies entirely inside k'_{α_0}. In the former case one domain is determined lying outside k_{α_0} and inside k'_{α_0}, in the latter case one or more domains.

We can now choose among the domains determined by k_α and k'_α in the following way for a certain segment of values α, starting at α_0 and stopping at α_F, every time a domain γ_α lying outside k_α and inside k'_α, in such a way, that to the boundary of each γ_α inside there is uniform convergence by the boundaries of the succeeding γ_α's, so that the domain γ_α continually contracts until at α_F it vanishes and its boundary is reduced to a point or arc of single curve.

To this end we choose in γ_{α_0} an arbitrary point, and fartheron we choose γ_α in such a way that this point lies inside it; this will be possible up to a certain value α'; we then stop at $^1/_2\,(\alpha_0 + \alpha') = \alpha''$. Next we choose inside the domain $\gamma_{\alpha''}$, determined in this way, an arbitrary point and for values of α, consecutive to α'', we determine γ_α in such a way, that the latter point lies inside it; if this is possible up to $\gamma^{(3)}$, we stop at $^1/_2\,(\alpha'' + \alpha^{(3)}) = \alpha^{(4)}$, and we continue this process in the same way until it leads after a denumerable number of steps to an end.

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[1]) Schoenflies, Jahresber. d. D. M. V. XV, p. 560.

[2]) id., Mathem. Ann. 62, p. 305.

This series of γ_α's can in general be chosen in different ways; the value α_F, where it ends, lies then either *before* α_r, or it coincides with α_r.

We shall now investigate such a series of domains γ_α more closely and we shall suppose that from α_0 as far as and inclusive of α_r no invariant point is situated on the curve k_α resp. k'_α.

If we describe the boundary of a domain γ_α in *opposite direction* of the hands we find it consisting alternately of arcs and points belonging to both k_α and to k'_α and which we shall call *dividing arcs* (which are of course closed sets of points) resp. *dividing points*, of arcs belonging only to k_α (being not closed sets of points) which we shall call *inner arcs of* k_α, and of curves belonging only to k'_α, which we shall call *inner arcs of* k'_α. To the above mentioned circuit of γ_α corresponds an order of succession of the inner arcs of k_α, belonging to a circuit of k_α *with* the hands, and an order of succession of the inner arcs of k'_α, belonging to a circuit of k'_α in *opposite direction* of the hands.

The part of k_α resp. k'_α, not belonging to the dividing arcs, dividing

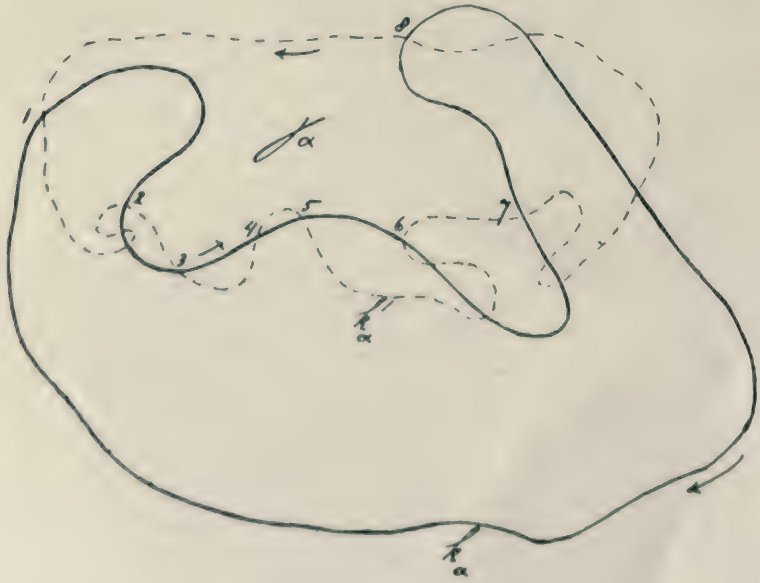

Fig. 1.

points, and inner arcs, consists of arcs (not closed sets of points), which we shall call *outer arcs of* k_α *resp.* k'_α. Between the endpoints of an inner arc of k_α runs an outer arc of k'_α, and inversely.

Each inner arc of k_α encloses with the corresponding outer arc of k'_α a domain lying inside k_α and inside k'_α, thus outside γ_α.

Each inner arc of k'_α encloses with the corresponding outer arc of k_α a domain lying outside k_α and outside k'_α, thus likewise outside γ_α. To this however *one* inner arc of k'_α forms an exception: it encloses with the corresponding outer arc of k_α a domain containing the inner domain of k_α and also the domain γ_α.

We shall now run along the boundary of γ_α in opposite direction of the hands, starting somewhere on that *special* inner arc of k'_α: in this way the row of dividing points and dividing arcs, or, as we shall call it, the *row of elements* of γ_α gets a first and a last element.

Accordingly in fig. 1. (which is special in as far as the elements appear only as dividing points and only in finite number) the elements are numbered from 1 to 8.

We look upon all those dividing points and dividing arcs as elements of k_α and we determine their images on k'_α. After that we suppose each outer arc to be laid along the corresponding inner arc by a continuous one-one representation; in this way all the images of the elements of γ find their places on its boundary and we investigate for each element of γ_α, whether when describing the boundary of γ_α in the opposite direction of the hands we find it gaining or losing on its image on k'_α [1]). (That a dividing arc as a whole gains or as a whole loses, follows from the absence of an invariant point). To an element of the first species we assign the sign d; to one of the second species the sign p. These signs are unequivocally determined, except in the case, that all the elements should have to have the same sign, for which we can then take either p or d.

We divide this row of elements into a succession of groups as extensive as possible, containing each only equal signs; then before the first and after the last element of each group k_α and k'_α lie outside each other during arcs, whose extension does not fall below a certain minimum.

If such a group lies between two inner arcs of the same curve, we call it an *even* group, and we represent it by two signs; if it lies between two inner arcs of different curves, we call it an *odd* group, which we represent by one sign.

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[1]) True, the difference in argument between an element and its image is determined only save an entire number of circuits; however a fixed choice for one of the elements includes a fixed choice for all. We can arrange that difference to be for all elements in absolute value smaller than a circuit; this is possible either in *one* or in *two* ways. In the first case is determined unequivocally, which elements gain on their images and which lose. In the second case they may be regarded arbitrarily as all gaining or as all losing on their images.

The number of the groups must of necessity be finite; thus belongs to each α a *row of signs* containing an *even* number of signs p or d, of which not more than two equal ones follow on each other.

Let us now first consider a value α_1, for which the curve k'_{α_1} possesses in the immediate vicinity of each of the dividing points and dividing arcs points on both sides of k_{α_1}. On either side of such a value α_1 there is a segment of values of α, to each of which belongs the same row of signs as to α_1. For when α converges to α_1, the corresponding set of dividing points and dividing arcs converges uniformly to the *whole* set of elements belonging to α_1.

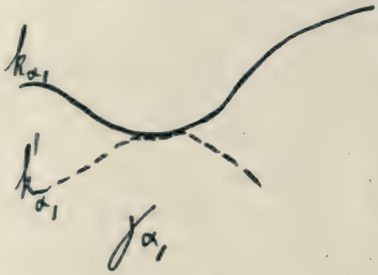

Fig. 2.

Let us next regard values α_1, where in the immediate vicinity of the elements which do not possess the just-mentioned property, the boundary of γ_{α_1} belongs exclusively to k_{α_1} or exclusively to k'_{α_1} (see fig. 2). For values α differing sufficiently little from that α_1 the corresponding set of elements uniformly differs indefinitely little from a *part* of the set of elements corresponding to α_1 (which *part* can be different for different α's). However, in such a part only even groups can be non-represented, and farther even groups belonging to that part are approximated by even groups and odd ones by odd ones.

Thus for the two regarded species of values α_1 within a certain vicinity each row of signs is obtained out of the row of α_1 by suppression of a certain number of pairs of equal successive signs.

We shall now understand by the *reduced row* of a given row of signs that one, which is obtained out of it by checking off a pair of equal successive signs, and repeating this process, until it is no longer possible. [1])

Thus e.g. of $p\ d\ p\ d\ d\ p\ d\ p\ p$

the reduced row of signs is p.

---

[1]) That this reduced row of signs is determined unequivocally is evident e.g. as follows: Let in a plane with rectangular system of coordinates p mean: *semi-revolution about the point* $(+1,0)$, and d: *semi-revolution about the point* $(-1,0)$, and let an arbitrary row of signs represent the product of the operations indicated by the signs. Different reduced rows of sign then furnish different results, and an arbitrary row of signs is equivalent to its reduced one.

We can now resume our results concerning the two regarded species of values a_1 as follows:

For each of these values a_1 the reduced row of signs is invariant within a certain vicinity.

We have now still to investigate a third species of values a_1, namely those for which dividing points appear, in whose immediate vicinity k_{α_1} and k'_{α_1} do not intersect each other, whilst the boundary of γ_{α_1} belongs on one side of that dividing point to k_{α_1}, on the other side to k'_{α_1}.

Such a dividing point may be endpoint of a *recurrent arc*, i. e. of an arc along which k_{α_1} and k'_{α_1} coincide, but in a direction, which corresponds for one of the two, but not for the other, to the sense of circuit of γ_{α_1}.

We shall now confine ourselves first to such values a_1 of the third species, as for all dividing points characterizing them as such possess that recurrent arc, and that in such a manner that in the immediate vicinity of it k_{α_1} and k'_{α_1} come on either side of each other (comp. fig. 3, where PQ is the recurrent arc and to the left of P the curves k_{α_1} and k'_{α_1} can be supposed to wind an infinite number of times round about each other, when approaching to P).

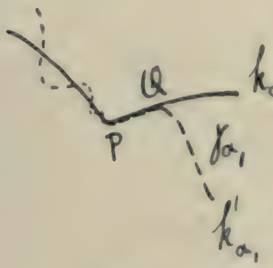

Fig. 3.

For values a differing sufficiently little from a_1 the corresponding set of elements uniformly differs indefinitely little from the sum of a *part* (with the same properties as for values a_1 of the second species) of the set of elements corresponding to a_1 and a *part* of the recurrent arc. On account of the absence of an invariant point on that arc here again the reduced row of signs must within a certain vicinity of a_1 be the same as that of a_1.

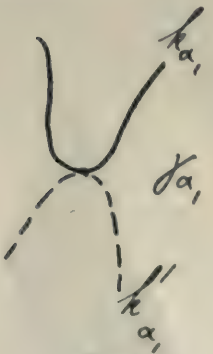

Fig. 4.

There remain still the values a_1 of the third species having dividing points characterizing them as such, which either possess *no* recurrent arc, or such a one that in its immediate vicinity the curves k_{α_1} and k'_{α_1} lie only on one side of each other (See fig. 4).

We here see clearly, that the proof for the invariability of the reduced row of signs *does* hold for a segment of values a *following* on a_1, but not for one preceding a_1.

We can however regard in this case of exception the domain γ_{α_1} as belonging to a *set of domains* G_{α_1}, whose character is that of a domain γ_{α}, not being in that case of exception, on whose boundary in one or more points or arcs an inner arc of k_{α} and an inner arc of k'_{α} touch each other without intersecting each other. An example is given in fig. 5, where γ_{α_1} with γ'_{α_1} and γ''_{α_1} composes the indicated set of domains G_{α_1}.

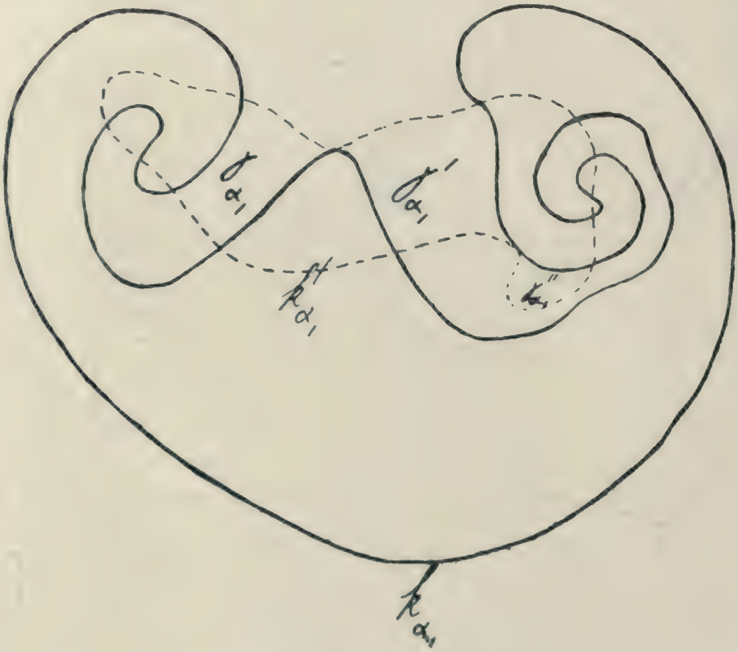

Fig. 5.

In the same way as for a domain γ_{α} we can define for a G_{α} the row of signs and the reduced row of signs.

For values of a preceding a_1 and converging to a_1 the boundary of γ_{α} converges uniformly to that of G_{α_1}, and *for a certain segment of values a preceding a_1 the reduced row of signs of γ_{α} is the same as that corresponding to G_{α_1}*.

The end we have in view is to prove that we can choose the successive domains γ_{α} in such a way, that for not one of those domains the reduced row of signs becomes $p\,d$.

If k_{α_0} and k'_{α_0} strike against each other on their outside, then we have for γ_{α_0} only one choice, for which the row of signs is pp (or $d\,d$) and the reduced row of signs *zero*, thus *not* $p\,d$.

If k_{α_0} lies entirely on or inside k'_{α_0}, then there is among the choices possible for γ_{α_0} certainly one whose row of signs is either $p\,p$

or *dp*, and the reduced row of signs either *zero* or *d p*, so again *not p d*.

We can thus at all events take care that for γ_{α_0} the reduced row of signs is *not p d*.

We now continue the succession of γ_α's in an arbitrary way according to the method given above, until after a certain finite segment of values α a first α appears, for which the reduced row of signs changes. Then we have certainly there a value α which is in the case of exception, and which we call α_{u_1}. We there have a $G_{\alpha_{u_1}}$, which breaks up into a set of domains $\gamma_{\alpha_{u_1}}$, and with each of these we may continue the succession of the γ_α's. We know that the reduced row of signs of $G_{\alpha_{u_1}}$ is *not pd*, and we shall show how from this ensues that for at least *one* of the $\gamma_{\alpha_{u_1}}$'s the reduced row of signs is *not p d*.

As a breaking up of G_α into several γ_α's by contact points or contact arcs can always be reduced to divisions into *two* γ_α's by contact in a single point, we have but to show that if in the latter case the two composing domains γ_α possess the reduced row of signs *pd*, G_α must also have that same reduced row of signs.

Let to that end in fig. 6 R be the point of contact which makes the division; let I be the composing domain whose boundary with the assumed sense of circuit passes in R from k_α to k'_α; then in II it passes in R from k'_α to k_α.

On the boundary of I two elements P_1 and P_2 can now be indicated, whose images on k'_α lie between P_1 and P_2.

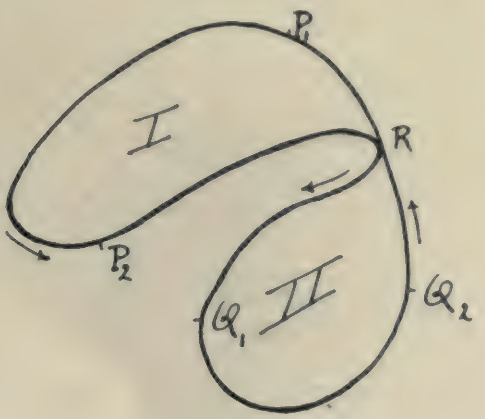

Fig. 6.

Likewise on the boundary of II we can choose two elements Q_1 and Q_2 whose images on k'_α lie between Q_1 and Q_2.

The element P_1 cannot coincide with R; for then it would be evident when describing the boundary of G_α as a whole, that all the elements of II had their images on k'_α on the same outer arc of II.

Neither can Q_2 coincide with R.

Now the image of R lies on k'_α between P_1 and Q_2, thus within the arc $P_1\,R$ as well as within the arc $R\,Q_2$ of k'_α. So R gets for the domain I the sign d and for the domain II the sign p.

We must now distinguish three cases: *the special inner arc of* k'_α namely appears as such either in I or in II or (if it contains R) in neither of the two. We shall continue the proof only for the first case; the other two can be treated analogously.

By the point R the row of signs of G_α is broken up into three successive parts, which we shall call ϱ, σ and τ; then the row of signs of I becomes

$$\varrho\ d\ \tau,$$

and that of II

$$p\ \sigma.$$

The reduction of the row of signs of II, i.e. of $p\,\sigma$, having to give $p\,d$, the reduction of σ must give d.

Thus by substituting in an arbitrary row of signs a σ for a d, its reduced row of signs remains unchanged.

However, pd being the reduction of the row of signs of I. i.e. of $\varrho\,d\,\tau$, it is also the reduction of $\varrho\,\sigma\,\tau$, i.e. of the row of signs of G_α, the property which we had to demonstrate.

So we can choose $\gamma_{\alpha_{u_1}}$ in such a way, that its reduced row of signs is *not* pd, and, starting from that, we can continue the succession of γ_α's arbitrarily until in this way after a certain segment of values α the row of signs would change for the first time for α_{u_2}. However, we can then again choose $\gamma_{\alpha_{u_2}}$ in such a way that its row of signs is *not* pd, and we can keep going on in this way. If an α_{u_ω} is reached as the limit of the α_u's, then if the case of exception appears also for that, it can be treated similarly; we can choose $\gamma_{\alpha_{u_\omega}}$ thus, that its reduced row of signs is *not* pd, and we can continue the succession of γ_α's with this property till a value $\alpha_{u_{\omega+1}}$ is reached. The whole set of α_u's must, however, be denumerable, and finally α_F is reached with a γ_{α_F}, whose reduced row of signs is *not* $p\,d$, thus whose row of signs itself is *not* $p\,d$.

On the other hand: of a γ_{α_F} on whose boundary lies no invariant point, the row of signs must precisely be pd. Thus the assumption, that from α_0 up to and inclusive of α_F no invariant point appears, leads to an inconsistency, and we have proved:

THEOREM 1. *A continuous one-one transformation in itself with invariant indicatrix of a singly connected, twosided, closed surface possesses at least one invariant point.*

The above given proof fails for a transformation with inversion of the indicatrix; on the contrary, according to that proof we can show how such transformations may easily be constructed without invariant point.

For then the curves k_α and k'_α have the same sense of circuit, and with the aid of a method of representation of SCHOENFLIES [1]) we can arrange them to possess for all values α between α_0 and α_F only two points of intersection whilst originally k_{α_0} lies inside k'_{α_0}. Let us now regard the part of the boundary of γ_α belonging to k_α, then fig. 7 shows how the image of that arc can begin to

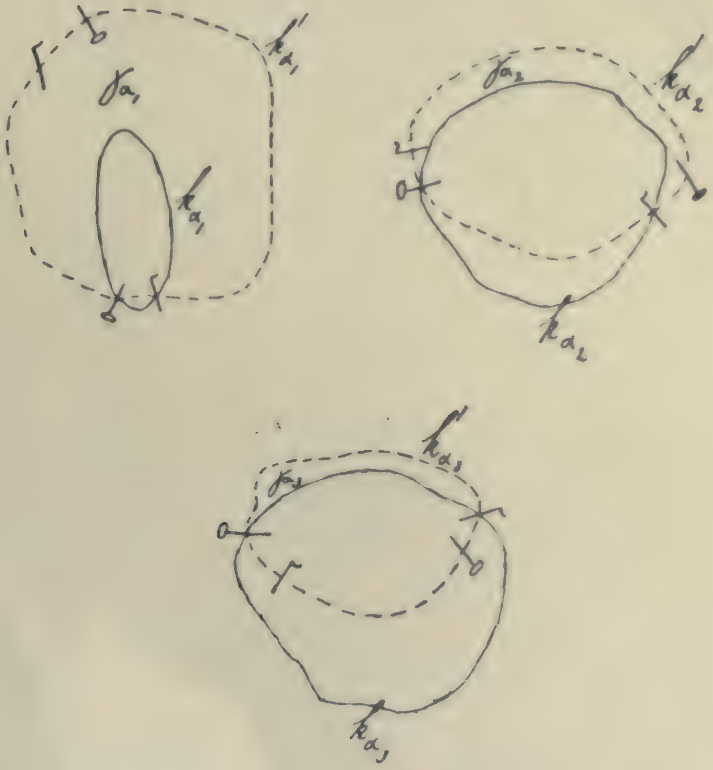

Fig. 7.

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[1]) Mathem. Ann. 62, p. 319—324.

have its endpoints on the boundary of γ_x, but how it can lateron withdraw its endpoints from that boundary and fartheron remain entirely outside it, without an invariant point having to appear.

We thus formulate:

THEOREM 2. *A continuous one-one transformation in itself with inversion of the indicatrix of a singly connected, twosided, closed surface does not necessarily leave a point invariant*[1]).

An elementary special case of theorems 1 and 2 is furnished by a sphere in ordinary space, having always two invariant points for congruent transformations in itself, but not necessarily one for symmetric transformations in itself.

In the formulation of theorem 1 the restriction implied in the word *closed* is not superfluous; for, an ordinary Cartesian plane has in an arbitrary translation a continuous one-one transformation in itself with invariant indicatrix, *without an invariant point.*

Neither is superfluous the condition of *single connection*; for the ordinary tore of Euclidean space has in an arbitrary rotation about its axis a continuous one-one transformation in itself with invariant indicatrix *without an invariant point.*

The restriction of *twosidedness*, however, can be cancelled.

We can, namely, bring the points of a onesided, singly connected, closed surface into a continuous one-two correspondence with those of a twosided one; to an indicatrix on the onesided surface then correspond two opposite indicatrices on the twosided one. On the ground of such a correspondence answer to a continuous one-one transformation in itself of the onesided surface two such transformations in itself of the twosided one, so that for one of them the indicatrix remains invariant, whilst it is inverted for the other one. As for the former at least one point remains invariant, for both at least one pair of points and for the transformation of the onesided surface at least one point remains invariant.

As farthermore for that transformation of that onesided surface we cannot speak of remaining invariant or inversion of the indicatrix, we can formulate:

THEOREM 3. *A continuous one-one transformation in itself of a singly connected, onesided, closed surface leaves at least one point invariant.*

An elementary special case of theorem 3 we find in an arbitrary plane, real-projective transformation having at least one invariant point.

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[1]) For a closed *line* of theorems 1 and 2 exactly the contrary holds: here a transformation with invariant indicatrix can exist without an invariant point; but with inverted indicatrix such a transformation is impossible.

Physics. — *"On the course of the isobars for binary systems II."* By Prof. PH. KOHNSTAMM. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of February 27, 1909).

8. The point $x=x_0$, $v=0$, the signification of which for the course of the lines $\frac{dp}{dv}=0$ and $\frac{dp}{dx}=0$ we set forth in the preceding paper (These Proc. 599), is also an exceptional point for the isobars themselves. If we approach this point along the line $x=x_0$, coming from large volumes, the pressure is first zero, ascends then to a maximum, at least for positive a, after which it passes again through zero, and continues to descend to $-\infty$, as appears easily from the formula $\frac{MRT}{v}-\frac{a}{v^2}$. If, on the other hand, we arrive at the point $x=x_0$, $v=0$ along the line $v=b$, we find for the pressure the value $+\infty$. Also all the intermediate isobars pass through this point, as appears when we substitute $b=\frac{db}{dx}x+\frac{1}{2}\frac{d^2b}{dx^2}x^2$ and $v=\left(\frac{dv}{dx}\right)_p x+\frac{1}{2}\left(\frac{d^2v}{dx^2}\right)_p x^2$ in the equation for the isobar, so assuming the point $x=x_0$, $v=0$ as origin of coordinates. If further we put $\left(\frac{dv}{dx}\right)_p=\frac{db}{dx}$, we get, disregarding the higher powers:

$$p=\frac{1}{x^2}\left\{\frac{2\,MRT}{\frac{d^2v}{dx^2}-\frac{d^2b}{dx^2}}-\frac{a}{\left(\frac{db}{dx}\right)^2}\right\}$$

and so, however small x be taken, we can find a point for every value of p satisfying the equation. When a is positive the condition for this is that $\frac{db}{dx}=\frac{dv}{dx}$, so that the isobar touches $v=b$, and further $\frac{d^2v}{dx^2}>\frac{d^2b}{dx^2}$, so the isobar has a smaller radius of curvature than $v=b$, and so has greater volume with equal x.

9. What was said in 7 and 5 enables us to indicate the course of the isobars in the neighbourhood of $x=x_0$, $v=0$. Coming from the said point and touching there $v=b$ (and so also $\frac{dp}{dv}=0$) an isobar for a high negative value of p will soon intersect the line

$\frac{dp}{dv}=0$. For as was proved in 5, $\frac{dp}{dv}=0$ lies here at smaller volumes than $\frac{dp}{dx}=0$, and so in the region where $\frac{dp}{dx}$ is positive. The line $\frac{dp}{dx}=0$ gives the minimum value of the pressure for every definite x, and so this minimum value becomes constantly higher towards the right, or in other words an isobar of a certain negative value of p cannot penetrate further to the right than that x, for which this value is reached on $\frac{dp}{dv}=0$. At the intersection with $\frac{dp}{dx}=0$ the isobar is // the x-axis, and afterwards it reaches the line $x=x_0$. The course outside this quadrant has no physical significance. So we get a course as fig. 10 presents for an isobar very close to $x=x_0$.

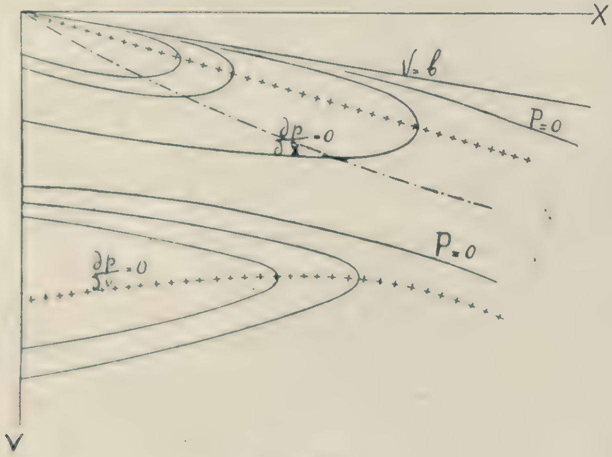
X
V
V=b
P=0
$\frac{\partial p}{\partial x}=0$
P=0
$\frac{\partial p}{\partial v}=0$

Fig. 10.

But not all the isobars originating from $x=x_0$, $v=0$ will present this course. The question, however, what the shape of the others is, and where the limit lies between the different kinds, can only be discussed when we have gained a complete survey of the points of intersection of $\frac{dp}{dx}=0$ and $\frac{dp}{dv}=0$, also of those lying at a great distance.

10. The results obtained up to now are pretty well independent of the question whether b is a linear, or a quadratic function of x, but now we must distinguish between these two suppositions. For it is clear that for points lying considerably to the right many

quantities will get an entirely different value depending on whether b increases with x or with x^2. Thus the critical temperature becomes infinite in the first case, in the second it approaches a finite amount, the critical pressure becomes finite in the first case, zero in the second, and also the situation of $\frac{dp}{dv} = 0$ with respect to $\frac{dp}{dx} = 0$ is quite different in one case from that in the other. For if we substitute in the equation:

$$F(v) = -\frac{dp}{dv} = \frac{MRT}{(v-b)^2} - \frac{2a}{v^3}$$

the value of $v-b$, as it holds for $\frac{dp}{dx} = 0$, we get:

$$F(v) = \frac{\frac{da}{dx}}{v^2 \frac{db}{dx}} - \frac{2a}{v^3}$$

Now we may put $a_1 x^2$ for a for very great value of x, $2a_1 x$ for $\frac{da}{dx}$, and $2b_1 x$ or b_1 for $\frac{db}{dx}$ depending on whether we assume the quadratic or the linear form for b. In the latter case:

$$F(v) = \frac{2a_1 x}{v^2} \left(\frac{v - b_1 x}{b_1 v} \right)$$

so positive, so that $\frac{dp}{dx} = 0$ is found in the region where $\frac{dp}{dv}$ is negative. In the former case we get:

$$F(v) = \frac{a_1}{v^2} \left(\frac{v - 2b_1 x^2}{b_1 v} \right)$$

so that $\frac{dp}{dx} = 0$ is found in the region were $\frac{dp}{dv}$ is negative (the stable region of the mixtures taken as homogeneous) only if $v > 2b$, which according to the known properties of the isotherm comes to the same thing as that the pressure in the minimum $\left(\frac{dp}{dv} = 0\right)$ is positive, or the temperature higher than $\frac{27}{32}$ of the critical temperature.

11. Let us for the present confine ourselves to the supposition of a quadratic function. So in the case which is still under consideration that there is minimum critical temperature and yet $a^2_{12} > a_1 a_2$,

no point of intersection of $\frac{dp}{dx}=0$ and $\frac{dp}{dv}=0$ will occur for very low temperature in the region on the right of x_0. For, as VAN DER WAALS has demonstrated (These Proc. June 1908) for such a point of intersection the equations

$$\left.\begin{aligned} MRT &= 2\frac{a}{b}\frac{b}{v}\left(1-\frac{b}{v}\right)^2 = \frac{\frac{da}{dx}}{\frac{db}{dx}}\left\{1-\frac{b\frac{da}{dx}}{2a\frac{db}{dx}}\right\}^2 \\ v &= \frac{2a\frac{db}{dx}}{\frac{da}{dx}} \end{aligned}\right\} \quad . \quad . \quad (1)$$

hold, so for very low temperature a point of intersection is only possible in the neighbourhood of an x, where either $\frac{da}{dx}=0$ or the critical pressure is stationary. Both these possibilities, however are not realised here, for as we shall show later on, a minimum critical temperature at the same time with $a^2_{12} > a_1a_2$ is only possible for a relative position of the lines a and b as indicated in fig. 11, i. e.

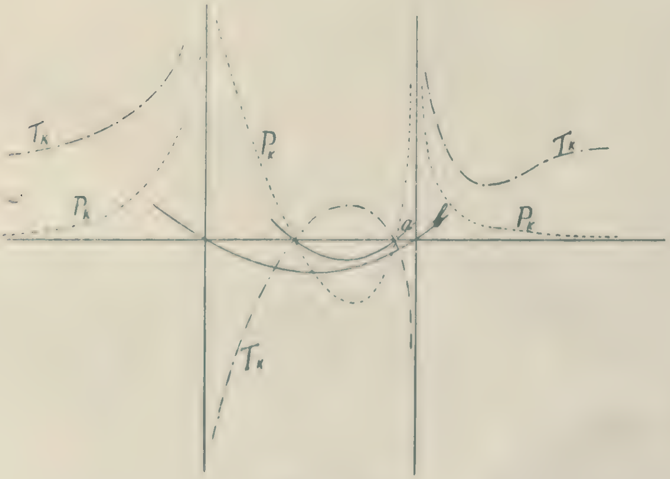

Fig. 11.

the point a_1 on the left of b_1 and $\frac{da}{dx}=0$ on the right of $\frac{db}{dx}=0$. Now for b_1 and b_2 the critical pressure is infinite, for a_1 and a_2 it is zero; also for $x = + \infty$ and $x = - \infty$. The equation $p_k = \frac{a}{b^2}$ being of the fourth degree in x, no more than 4 values of x can ever be found for a certain value of p_k. So no maximum or minimum of the critical pressure can occur on the right of b_1.

Here we interrupt the train of our reasoning for a moment, to show that in the case considered a minimum critical temperature must occur. As the equation:

$$\frac{dT_k}{dx} = \frac{b\frac{da}{dx} - a\frac{db}{dx}}{b^2} = 0$$

gives an equation of the third degree, we might expect that 3 values of x which make T_k stationary, could be found for every system in the complete diagram of isobars. But as for very great values of x always $b\frac{da}{dx} = a\frac{db}{dx} = a_1 b_1 x^3$, one root appears always to lie at infinity, and there are at most two roots for finite x. One of them lies between a_1 and a_2, where T_k becomes $= 0$, the other lies on the right of b_1. For in our case we may write the equation for a and b:

$$a = a_1 (x - x_0)^2 - a_2 \qquad b = b_1 x^2 - b_2$$

so

$$\frac{da}{dx} = 2a_1 (x - x_0) \qquad \frac{db}{dx} = 2b_1 x\,.$$

$\frac{dT_k}{dx}$ has the sign of $b\frac{da}{dx} - a\frac{db}{dx}$, and so of:

$$2a_1 b_1 x^2 (x - x_0) - 2a_1 b_1 x (x - x_0)^2 = 2a_1 b_1 x^2 x_0 - 2a_1 b_1 x x_0^2$$

so $\frac{dT_k}{dx}$ is positive for high values of x, which proves the presence of a minimum critical temperature in connection with the value $+ \infty$ for $b = 0$.

12. Let us now return to our diagram of isobars. We can now represent it fully for low temperatures, now that we have seen that there will be no intersection of $\frac{dp}{dx} = 0$ and $\frac{dp}{dv} = 0$ in this case. We have only to add the observation that the value of the pressure on the line $\frac{dp}{dv} = 0$ approaches indefinitely to zero for very great value of x, however small the value of T is, if only not quite zero.

For $\frac{MRT}{v-b}$ is in inverse ratio to x, and $\frac{a}{v^2}$ to x^2. So it follows from this that all the negative isobars starting from the point $x=x_0$, $v=0$ will have the shape we indicated before. The line $p=0$ will intersect the line $\frac{dp}{dv}=0$ at infinite distance. To this isobar, however, also the branch belongs starting from the point $p=0$ on the line $x=x_0$, and also the line $v=\infty$. For a positive pressure the isobar consists of two separate branches. One of them, starting from the point $x=x_0$, $v=0$ remains confined to smaller volumes than $p=0$, the other starting from a point on the line $x=x_0$, arrives somewhere on the vapour branch of $\frac{dp}{dv}=0$, with ascending value of v and x, has a tangent there parallel to the v-axis, and returns again to the line $x=x_0$, now on the other side of the maximum pressure. So we get fig. 10 for the complete course of the isobars.

13. How will this figure be modified with increase of temperature. Let us consider the temperature which is $\frac{27}{32}$ of the minimum critical temperature. From equation (1) on page 802 follows that we may expect a point of intersection at a volume $v=2b$ and a temperature $\frac{27}{32}T_k$ for the mixture with minimum critical temperature $\left(\text{where } a\frac{db}{dx}=b\frac{da}{dx}\right)$. The line $\frac{dp}{dv}=0$ lying at smaller volumes than the line $\frac{dp}{dx}=0$ for very great values of x, as we saw in 10, there must be another point of intersection more to the right. It is clear that these points of intersection have arisen by a contact of $\frac{dp}{dx}=0$ and $\frac{dp}{dv}=0$, and that the two points of intersection have moved from this point of contact in opposite direction. For as the equations for the points of intersection are of the first degree with respect to T and v, it is not possible that two points of intersection lying beside each other move in the same direction; for then we should find different values of T for the same value of x. In the point of intersection lying most to the left the pressure is 0, from which it already follows that there must be another point of intersection; for the pressure finally verging again to zero towards the right, there must be a point between where the pressure has reached its lowest value on

the line $\frac{dp}{dv}=0$. So this point is really a minimum of pressure. Now the diagram of isobars has changed in this (fig. 12) that a loop-line

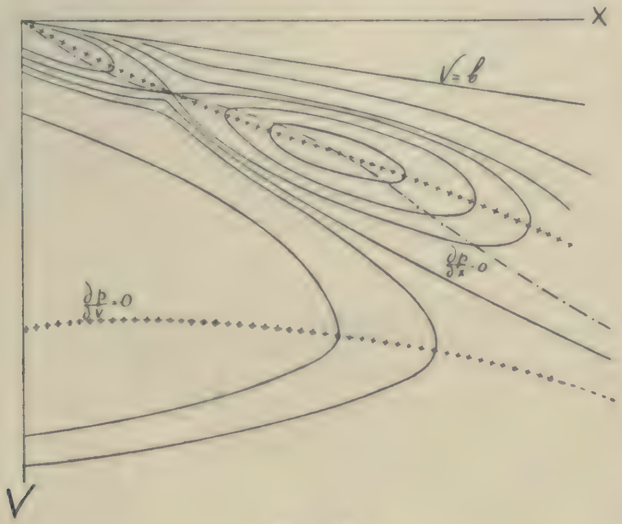

Fig. 12.

has made its appearance, as we see immediately from the fact that the direction of the tangent of the isobar $p=0$, passing through the point of intersection of $\frac{dp}{dv}=0$ and $\frac{dp}{dx}=0$ becomes indeterminate in this point. The two branches of this loop-line start, of course, one from the point $x=x_0$, $v=0$, the other from the point on the line $x=x_0$, where $p=0$. They pursue their course through the double point towards infinity, just as the branches of $p=0$ in figure 10. Now too, the positive isobars have the same course as indicated there. The negative isobars, however, at least part of them, have broken up into two parts, a branch on the left of the mixture with minimum critical temperature, which has again the same course as in fig. 10, and a branch on its right, forming a closed curve round the second point of intersection of $\frac{dp}{dx}=0$ and $\frac{dp}{dv}=0$. Only for isobars for a larger negative value than that in the last-mentioned point there exists only one branch.

It is clear what will be the course for intermediate temperatures. It follows then again from the given equation that the pressure will be negative in the double point lying then at a value of x where $b\frac{da}{dx}>a\frac{db}{dx}$. So we have a loop-line, which itself runs again as a closed line round the second point of intersection of $\frac{dp}{dx}=0$ and $\frac{dp}{dv}=0$.

14. At a temperature higher than $\frac{27}{32}$ of the minimum critical temperature, there is positive pressure in the double point. For the double point continually proceeds in the same direction; so $\frac{b\frac{da}{dx}}{a\frac{db}{dx}}$ or $\frac{b}{v}$ constantly decreases during this movement and now the expression:

$$\frac{MRT}{MRT_k}=\frac{27}{8}\frac{b\frac{da}{dx}}{a\frac{db}{dx}}\left(1-\frac{b\frac{da}{dx}}{2a\frac{db}{dx}}\right)^2=\frac{27}{8}n\left(1-\frac{n}{2}\right)^2$$

has a value 0 for $n=0$ and $n=2$, a maximum for $n=\frac{2}{3}$; between $n=1$ (the x of the minimum critical temperature) and $n=\frac{2}{3}$ the righthand member is, therefore, greater than $\frac{1}{4}$ and so $T>\frac{27}{32}T_k$, so that the pressure in the double point is positive. For $n=\frac{2}{3}$ the double point lies exactly at $T=T_k$ or $v=3b$, so in the point of $\frac{dp}{dv}=0$ where this line, which then has split up, has its tangent // v-axis. At still higher temperature the double point of p gets on the vapour branch of $\frac{dp}{dv}=0$, and disappears at the temperature at which $\frac{da}{dx}=MRT\frac{db}{dx}$ for $x=x_0$, as is indicated in fig. 9. So long as the double point continues to lie on the liquid branch, that branch of the isobar, which comes from $x=x_0$, $v=0$, passes through the double point, meets the vapour-branch of $\frac{dp}{dv}=0$ at larger x, where its tangent becomes // v-axis, and then runs back to a point of the line $x=x_0$ for greater value of v than that of the maximum pressure on the straight line mentioned. The other branch of the loop-isobar comes from a point of this line with smaller pressure than the maximum pressure, and having passed the double point it remains at smaller volumes than $\frac{dp}{dx}=0$. The course of the other isobars only undergoes modification as regards the isobars which intersect the line $\frac{dp}{dx}=0$ on the right of the double point. Near the double point positive isobars are found at this temperature. They come from a point on the line $x=x_0$ at larger volume than the largest that the loop-isobar has in common with this line. They are // v-axis on the vapour branch of $\frac{dp}{dv}=0$, then they run back to smaller x, they are again // v-axis on the liquid branch of $\frac{dp}{dv}=0$, and // x-axis on $\frac{dp}{dx}=0$, after which they proceed towards infinity between the last-mentioned line and the loop-isobar. So we have again got isobars here as in the rigthand part of VAN DER WAALS' diagram of isobars (Fig. 13).

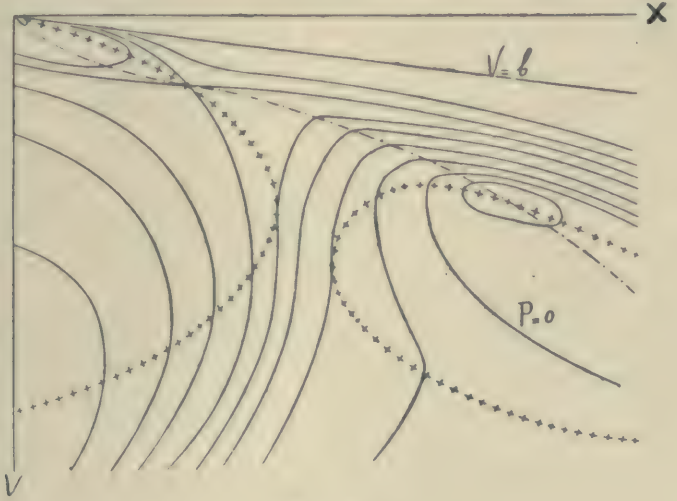

Fig. 13.

When we ascend above the critical temperature, so that $\frac{dp}{dv}=0$ breaks up into a righthand part and into a lefthand part, this involves only that part of the isobars no longer possess the retrograde portion, because the two points of intersection with $\frac{dp}{dv}=0$ have coincided, and then have become imaginary. The last isobar which has the shape described here, is that for $p=0$, the line at infinity included. It then runs from the line $x=x_0$ to the vapour branch of $\frac{dp}{dv}=0$

on the extreme right side of the figure, returns to a point on the liquid branch of $\frac{dp}{dv}=0$, and then intersects $\frac{dp}{dx}=0$ The negative isobars, which have their point of intersection with the liquid branch of $\frac{dp}{dv}=0$ still further to the right, again form closed rings round the second point of intersection of $\frac{dp}{dv}=0$ and $\frac{dp}{dx}=0$. These closed rings do not disappear until the temperature has been raised so high that the value $\frac{27}{32}\frac{a_1+a_2-2a_{12}}{b_1+b_2-2b_{12}}$ has been reached, which may take place either above the minimum critical temperature of the system or not above it, in the first case again either at higher temperature or not at higher temperature than that at which the point of intersection of $\frac{dp}{dv}=0$ and $\frac{dp}{dx}=0$ has shifted from the liquid branch to the vapour branch. So different combinations may present themselves, which, however, do not differ in essential points, and which the reader can easily imagine for himself.

15. At temperatures at which the double point lies on the vapour branch, the loop-isobar, starting from $v=0, x=x_0$ passes first through the liquid branch of $\frac{dp}{dv}=0$, where its direction is // v-axis, then through the double point, after which it reaches the line $x=x_0$. The second branch of the loop-isobar comes from the line $x=x_0$, and after having passed through the double point, it pursues its course always at smaller volumes than $\frac{dp}{dv}=0$ and $\frac{dp}{dx}=0$. In the isobars with higher value of the pressure only this change has come that now a retrograde part appears in the branch at the small volumes for a number of isobars, whereas part of the isobars with lower value than the loop-isobar fail to have the retrograde portion in the branch starting from the line $x=x_0$. They do not get it until the value of the pressure has fallen so low that the righthand part of $\frac{dp}{dv}=0$ is intersected. When the temperature $\frac{a_1+a_2-2a_{12}}{b_1-b_2+2b_{12}}$ has been reached, this part of $\frac{dp}{dv}=0$ has vanished, and so also the retrogression of all these isobars. (fig. 14).

The last modification which our diagram may finally undergo, is when the temperature at which $\frac{da}{dx} = MRT \frac{db}{dx}$ for $x = x_0$, is reached. Our diagram then passes into the usual one, when this is drawn above the critical temperature, and as we have now to deal with the case of fig. 9, into the usual figure after the intersection of $\frac{dp}{dv} = 0$ and $\frac{dp}{dx} = 0$ has disappeared.

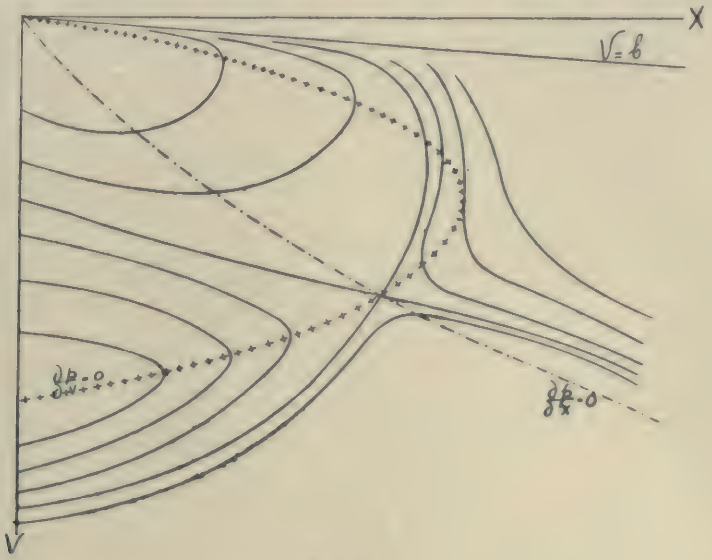
X
V=b
$\frac{\partial p}{\partial v}=0$
$\frac{\partial p}{\partial x}=0$
V

Fig. 14.

16. Now the course of the isobars for the case that a minimum critical temperature occurs at the same time with $a_{12}^2 > a_1 a_2$ is completely determined. Only this complication might possibly be met with — I have at least not succeeded in proving that it is impossible — that besides the discussed contact of $\frac{dp}{dv} = 0$ and $\frac{dp}{dx} = 0$, by which two points of intersection arise, another contact is found. As we saw before the points of contact which then arise will again have to move to opposite sides. Of the four points of intersection which there are in this case, the two inner ones will again coincide at still higher themperature, and give rise to contact. So the difference is confined to the region between the two temperatures of contact, and it has only influence on part of the isobars at small volumes. Thus of the series of isobars which pass round the point with minimum pressure on $\frac{dp}{dv} = 0$ as closed curves, there will

e. g. be one which assumes the shape of a ∞, and the isobars of still smaller value of p will have broken up into two branches each closed in itself (apart from the closed portion starting from $x=x_0$, $v=0$). C and D (fig. 15) are then the points of intersection which have newly appeared; the complication vanishes again in consequence of the coincidence of B and C. If the second point of contact should arise on the left of the point of intersection lying to the extreme left instead of on the right of B a similar result would be met with.

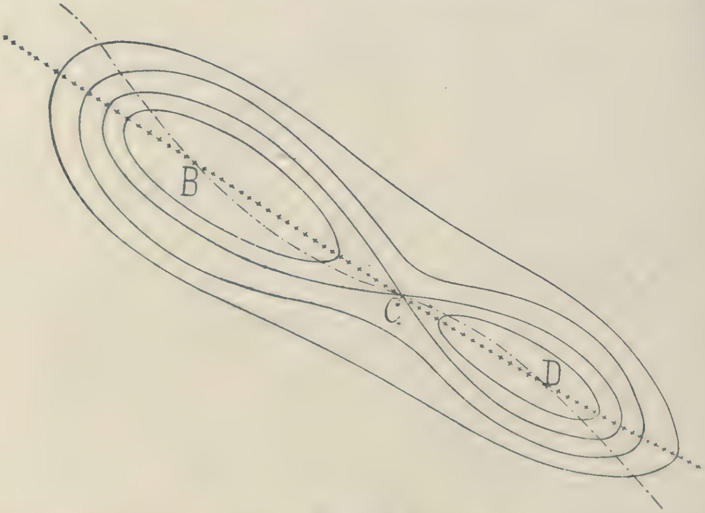

Fig. 15.

17. At first sight the diagrams of isobars obtained above seem to deviate considerably from the figure given by VAN DER WAALS. This is of course partly due to the different course of $\frac{dp}{dx}=0$. Partly, however, also to the fact that the figure loc. cit. only holds for temperatures, lying between $\frac{27}{32}$ of the critical temperature and the critical temperature itself. Therefore we find the closest resemblance with the figure loc. cit. in our figures for higher temperatures. That the resemblance also continues to exist at lower temperatures is immediately seen when we examine to what changes the figure l. c. is subjected with lowering of the temperature. First of all we have then the temperature:

$$\frac{27}{32}\frac{a_1+a_2-2a_{12}}{b_1+b_2-2b_{12}}.$$

As we saw above another point of intersection of $\frac{dp}{dx}=0$ and

$\frac{dp}{dv} = 0$ is found on the right below this temperature, round which point of intersection branches of isobars with negative value of the pressure pass as closed curves. For $\frac{27}{32}$ of the minimum critical temperature the loop-isobar will hold for the pressure 0, as we saw above. So it reaches the vapour branch of $\frac{dp}{dv} = 0$ only at infinity (fig, 16). For still lower temperature also the loop-isobar in the case of van der Waals is no longer closed round the point of intersection of $\frac{dp}{dx} = 0$ with the vapour branch of $\frac{dp}{dv} = 0$, but round the third point of intersection. Of course closed rings continue to run round

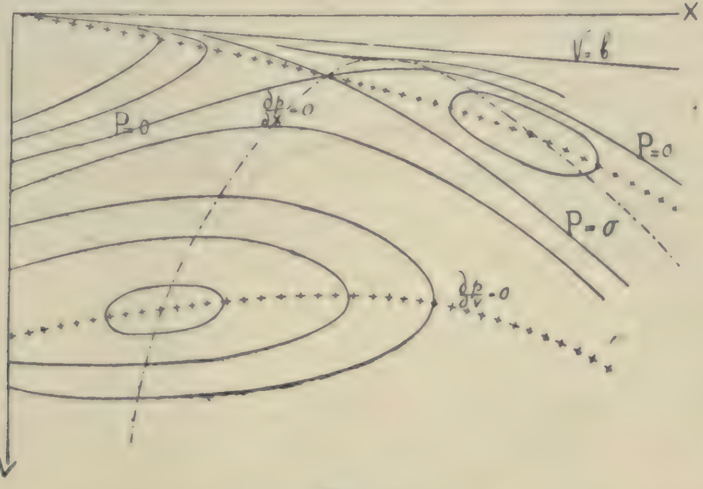

Fig. 16.

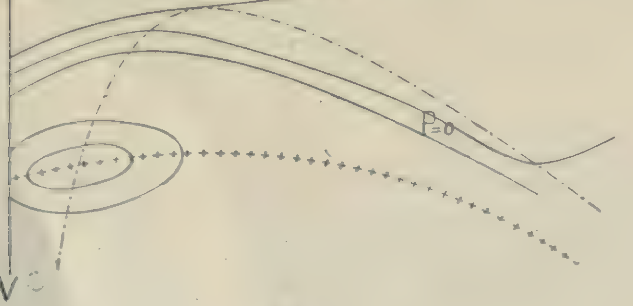

Fig. 17.

the first-mentioned point of intersection, which continues to distinguish the figure from the figures given by us. At still lower temperature the two points of intersection with the liquid branch of $\frac{dp}{dv}=0$ may coincide. It is true that this clashes with the thesis concerning the contact of $\frac{dp}{dx}=0$ and $\frac{dp}{dv}=0$, mentioned in the beginning of the previous communication, which gave rise to this investigation, but then this thesis holds only if b is a linear function of x and in this case the said point of intersection on the right does not make its appearance. If the two points of intersection have coincided, the loop-line and the closed rings at small volume have disappeared and only those at large volumes remain. (fig. 17). It is, however, also possible that the points of intersection continue to exist down to the absolute zero point, viz. when a minimum and a maximum occurs in the critical pressure. That this is possible for a quadratic function for b is shown by fig. 18, if we bear in mind that a and so the critical pressure never become zero now. In this case the points of intersection in the liquid branch continue to exist down to the lowest temperatures, their limiting situation is the value for x at which the critical pressure is stationary.

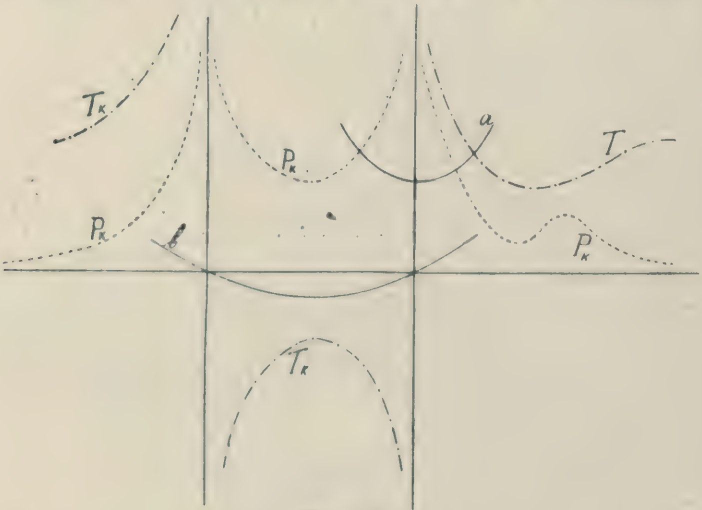

Fig. 18.

With this exception and with those exceptions which arise by the modified course of $\frac{dp}{dx}=0$, this diagram and ours harmonize.

In a following communication I hope to show that so long as no maximum critical temperature occurs, no other diagrams of isobars but those discussed are possible in the realizable region (also the unstable one) for whatever values of a, b and a_1, we combine.

Mathemathics. — *"On a class of differential equations of the first order and the first degree."* By Prof. W. KAPTEYN.

1. In the last meeting of this Academy Prof. J. DE VRIES gave a geometrical criterion for determining whether or not a given differential equation of the first order and the first degree may be reduced by a homographic substitution to a linear equation or to an equation of the form

$$\frac{dy}{dx}=\frac{N(x)y^2+P(x)y+Q(x)}{R(x)y+S(x)} \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

The object of this paper is to examine the general form of all those equations which by a homographic substitution may be reduced to the equation (1). It is evident that this general form will give at the same time all the equations which are reducible either to the general equation of RICCATI, or to the linear form.

2. Let the substitution be

$$x=\frac{a_1u+a_2v+a_3}{c_1u+c_2v+c_3}=\frac{\alpha}{\gamma} \qquad y=\frac{b_1u+b_2v+b_3}{c_1u+c_2v+c_3}=\frac{\beta}{\gamma} \quad . \; . \quad (2)$$

where a, b, c are constants, then the equation (1) is

$$\frac{dv}{du}=\frac{C[\beta^2N^*+\beta\gamma P^*+\gamma^2Q^*]-A\gamma[\beta R^*+\gamma S^*]}{\gamma B[\beta R^*+\gamma S^*]-D[\beta^2N^*+\beta\gamma P^*+\gamma^2Q^*]} \quad . \; . \; . \quad (3)$$

where

$$A=b_1\gamma-c_1\beta \qquad C=a_1\gamma-c_1\alpha$$
$$B=b_2\gamma-c_2\beta \qquad D=a_2\gamma-c_2\alpha$$

and

$$N^*=N\left(\frac{\alpha}{\gamma}\right),\ P^*=P\left(\frac{\alpha}{\gamma}\right),\ Q^*=Q\left(\frac{\alpha}{\gamma}\right),\ R^*=R\left(\frac{\alpha}{\gamma}\right),\ S^*=S\left(\frac{\alpha}{\gamma}\right)$$

Transforming now to parallel axes, taking as the new origin o coordinates the point where the lines $\alpha=0$ and $\gamma=0$ meet, we find the new equation by substituting

$$u=\frac{(a_2c_3)}{(a_1c_2)}+u' \;,\; v=\frac{(a_3c_1)}{(a_1c_2)}+v'$$

$(a_2c_3)=a_2c_3-a_3c_2$, etc.

In this way, we get

$$\alpha=a_1\,u'+a_2\,v' \;,\; \beta=b_1\,u'+b_2\,v'+\varrho=\beta'+\varrho \;,\; \gamma=c_1\,u'+c_2\,v'$$

ϱ being a constant, and

$$\begin{array}{ll} A = (b_1\, c_2)\, v' - c_2\, \varrho & C = (a_1\, c_2)\, v' \\ B = -(b_1\, c_2)\, u' - c_2\, \varrho & D = -(a_1\, c_2)\, u' \end{array}$$

$$N\left(\frac{\alpha}{\gamma}\right) = N\left(\frac{a_1\, u' + a_2\, v'}{c_1\, u' + c_2\, v'}\right) = N_0 \quad , \quad P\left(\frac{\alpha}{\gamma}\right) = P_0 \text{ etc.}$$

where $N_0\, P_0$ etc. are homogeneous functions of u' and v' of degree zero.

Hence, if we arrange according to the degrees of u' and v' the numerator takes the form

$$\begin{array}{l} \quad (a_1\, c_2)\, v'\, [N_0\, \beta'^2 + P_0\, \beta'\gamma + Q_0\, \gamma^2] \\ - (b_1\, c_2)\, v_1\, [R_0\, \beta'\gamma + S_0\, \gamma^2] \\ + \varrho(a_1\, c_2)\, v'\, [2\, N_0\, \beta' + P_0\gamma] \\ - \varrho(b_1\, c_2)\, R_0\, v'\gamma \\ + \varrho\, c_1\, [R_0\beta'\, \gamma + S_0\gamma^2] \\ + \varrho^2\, (a_1\, c_2)\, N_0\, v' \\ + \varrho^2\, c_1\, R_0\, \gamma \end{array}$$

and in the same way the denominator may be written

$$\begin{array}{l} \quad (a_1\, c_2)\, u'\, [N_0\, \beta'^2 + P_0\, \beta'\, \gamma + Q_0\, \gamma^2] \\ - (b_1\, c_2)\, u'\, [R_0\, \beta'\, \gamma + S_0\, \gamma^2] \\ + \varrho\, (a_1\, c_2)\, u'\, [2\, N_0\, \beta' + P_0\, \gamma] \\ - \varrho\, (b_1\, c_2)\, R_0\, u'\, \gamma \\ - \varrho\, c_2\, [R_0\, \beta'\gamma + S_0\, \gamma^2] \\ + \varrho^2\, (a_1\, c_2)\, N_0\, u' \\ - \varrho^2\, c_2\, R_0\, \gamma. \end{array}$$

If we examine these values it is evident that the equation (3) reduces to

$$\frac{dv'}{du'} = \frac{K_1 + M_2 + v'(N_2 + c)}{H_1 + L_2 + u'(N_2 + c)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where c represents a constant, H_1 and H_2 homogeneous functions of the first degree and $L_2\ M_2\ N_2$ homogeneous functions of the second degree.

From the values

$$\begin{array}{rl} H_1 = & -\varrho^2 c_2 R_0 \gamma \\ K_1 = & \varrho^2 c_1 R_0 \gamma \\ c\ = & \varrho^2 (a_1 c_2) N_0 \end{array}$$

we may readily induce that if, in (1) $R(x)$ is absent H_1 and K_1 must be zero and if in (1) $N(x)$ is absent, we have $c = 0$.

The preceding considerations furnish the inference that every homographic substitution applied to an equation (1), followed by a transformation to parallel axes through the point $\alpha = \gamma = 0$ gives necessarily an equation of the form (4).

3. Now we will show that where a differential equation of this form (4) is given, there always exists a homographic substitution by which this equation may be reduced to the form (1).

For let

$$u' = \frac{1}{y} \qquad v' = \frac{x}{y}$$

then we have

$$K_1 = K_1(u'v') = K_1\left(\frac{1}{y}, \frac{x}{y}\right) = \frac{1}{y} K_1(1, x)$$

$$M_2 = M_2(u'v') = M_2\left(\frac{1}{y}, \frac{x}{y}\right) = \frac{1}{y^2} M_2(1, x)$$

etc. Thus (4) reduces to

$$\frac{dy}{dx} = \frac{\{H_1(1,x)+c\}y^2 + L_2(1,x)y + N_2(1,x)}{\{xH_1(1,x) - K_1(1,x)\}y + xL_2(1,x) - M_2(1,x)} \quad . \quad . \quad . \quad (5)$$

which is of the same form as the differential equation (1).

4. Therefore we have proved this:

Theorem. The necessary and sufficient condition that a differential equation of the first order and the first degree, having a singular point in the origin of coordinates, may be reduced by a homographic substitution to an equation (1) is that it may be written in the form

$$\frac{dy}{dx} = \frac{K_1 + M_2 + y(N_2 + c)}{H_1 + L_2 + x(N_2 + c)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Corollary 1. The necessary and sufficient condition that a differential equation of the same kind may be reduced by a homographic substitution to an equation of Riccati is that it has the form

$$\frac{dy}{dx} = \frac{M_2 + y(N_2 + c)}{L_2 + x(N_2 + c)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Corollary 2. The necessary and sufficient condition that a differential equation of the same kind may be reducible by a homographic substitution to a linear equation is that it has the form

$$\frac{dy}{dx} = \frac{M_2 + yN_2}{L_2 + xN_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

5. With respect to the equation (8) we may remark that it is equivalent with

$$\frac{dy}{dx} = \frac{M_1 + y\,N_1}{L_1 + x\,N_1}$$

as the numerator and the denominator of the second member may be divided by the same homogeneous function of the first degree. In the special case that $L_1 = a_1 x + b_1 y$, $M_1 = a_2 x + b_2 y$, $N_1 = c_1 x + d_1 y$ the tangents to the integral curves in the different points of the line $y = mx$, meet in the pole

$$X = -\frac{a_1 + b_1 m}{c_1 + d_1 m} \qquad Y = -\frac{a_2 + b_2 m}{c_1 + d_1 m}$$

Hence the locus of these poles for all the rays of the pencil $y = mx$ is the polar line

$$\begin{vmatrix} X & Y & 1 \\ a_1 & a_2 & -c_1 \\ b_1 & b_2 & -d_1 \end{vmatrix} = 0$$

This is the case in the examples II—VI given by Prof. DE VRIES. As to the examples I and VII we have respectively

$$L_1 = x \qquad M_1 = x + 2y \qquad N_1 = \frac{xy^2 + y^3}{x^2}$$

$$L_1 = 0 \qquad M_1 = y \qquad N_1 = \frac{x^2}{y}$$

Physics. — "*Contribution to the theory of binary mixtures.*" XIV.

By Prof. J. D. VAN DER WAALS.

(DOUBLE RETROGRADE CONDENSATION).

Before proceeding to the discussion of the significance of negative value of ε_1 and ε_2, I shall make a few remarks to elucidate what was mentioned in the preceding contribution — and that chiefly on the shape of the surface of saturation in the cases represented by figs. 39 and 40, and the relative position of the three-phase-pressure with respect to the sections of that surface for given value of x.

In case of complete miscibility such a section of the surface of saturation consists of a vapour branch and a liquid branch, which have a continuous course, in which the pressure gradually increases with ascending T, and which for certain value of T, which may be indicated by T_r, pass into each other continuously. The pressure must then before have had a maximum on the liquid branch, and then decrease. It passes into the pressure of the vapour branch at T_r. This gradual merging of the two branches into each other continues to exist also for non-complete miscibility.

In the case of fig. 39 the upper sheet of the surface of saturation undergoes, however, first of all a modification, which, however, is confined to values of x between $(x_3)_g$ and $(x_2)_g$, when $(x_3)_g$ denotes the value of x for which on the righthand side of the closed dotted curve the tangent is normal to the x-axis, and in the same way $(x_2)_g$ the same thing on the lefthand side.

For a section between $(x_3)_g$ and $(x_2)_g$ the modification remains restricted between the two values of T which are determined by the closed dotted curve of fig. 39 for the temperature. Outside these values of x and T the upper sheet is, if not quite unmodified, yet of the usual shape. If we call the concentration of the vapour phase x_1, and that of the coexisting liquid phase x_2, this usual shape of the upper sheet is determined by the equation:

$$v_{12}\, dp = (x_1 - x_2) \left(\frac{d^2\zeta}{dx_2{}^2}\right)_{pT} dx_2 + \eta_{12}\, dT.$$

And if it were our purpose to determine the situation of the sheet of the three-phase-pressure with respect to the metastable and unstable sheet of the coexisting equilibrium between vapour and liquid, the above equation might serve this purpose. For along the circumference of the closed dotted curve of fig. 39 the value of $\frac{dx_2}{dT}$ is known. Thus to give an example, this quantity is positive in the lower part on the right hand of Q_1. And v_{12} being positive and $x_1 - x_2$ negative, we find from:

$$\left(\frac{dp}{dT}\right)_{123} = (-) + \left(\frac{\partial p}{\partial T}\right)_{x_{12}}$$

$\left(\frac{dp}{dT}\right)_{123} < \left(\frac{\partial p}{\partial T}\right)_{x_{12}}$. Hence in the righthand part the sheet of the three-phase-pressure lies below the metastable sheet — which, however, might be considered as having been known beforehand from the shape of a p,x-line at constant temperature for the equilibrium vapour-liquid. In the lefthand part the sheet of the three-phase-pressure lies on the other hand above the metastable sheet.

In a section normal to the x-axis just through Q_1 the sheet of the three-phase-pressure begins at Q_1 touching the metastable sheet, and in a section just through Q_2 there is contact at the end. But it would lead us too far to include all the metastable and unstable sheets in our consideration. To examine what the shape is of the stable part of the liquid sheet inside the dotted ring, and so of the upper part of the surface of saturation is, however, very necessary indeed.

If we take two points of the dotted ring lying on a level and if we call the value of x for the point lying on the right x_3 and for the point lying on the left x_2, then

$$v_{23}dp = (x_2 - x_3)\left(\frac{d^2\zeta}{dx_3^{\,2}}\right)_{pT} dx_3 + \eta_{23}dT$$

or

$$\frac{dp}{dT_{123}} = \left(\frac{\partial p}{\partial x}\right)_{23}\frac{dx_3}{dT} + \left(\frac{\partial p}{\partial T}\right)_{x_{23}}.$$

holds for the equilibrium between these two liquids for the point lying on the right.

In the second member the second term $\left(\frac{\partial p}{\partial T}\right)_{x_{23}}$ holds for the section for constant value of x, the shape of which section we will determine — in the first term of the second member we have omitted the index T to avoid great complication in our notation. The shape of the line of equilibrium between the two liquids is known of a p,x-section of the surface of saturation, if three-phase-pressure occurs. It is a curve which ascends steeply in the points 2 and 3, and reaches a maximum value between them. In the point 3 $\left(\frac{\partial p}{\partial x}\right)_{23}$ has a high negative value, and if $\frac{dx_3}{dT}$ is positive, which is the case on the lower side of the righthand half of the dotted curve, $\frac{dp}{dT_{123}}$ is smaller than $\left(\frac{\partial p}{\partial T}\right)_{x_{23}}$. On the lefthand part of the lower side $\frac{dx_3}{dT}$ is negative, but there $\left(\frac{\partial p}{\partial x}\right)_{23}$ is positive, so that we arrive at the same result there. On the upper side we come to the opposite conclusion. So if we draw the upper branch of the section of the surface of saturation, such a modification must be applied between the limits of the temperature, which are to be derived from the dotted curve of fig. 39, that the three-phase-pressure lies below this curve — which was, indeed, a priori to be expected. And by a comparison of the two equations:

$$\frac{dp}{dT_{123}} = \left(\frac{\partial p}{\partial x}\right)_{23}\frac{dx_3}{dT} + \left(\frac{\partial p}{\partial T}\right)_{x_{23}},$$

and

$$\frac{dp}{dT_{123}} = \left(\frac{\partial p}{\partial x}\right)_{13}\frac{dx_3}{dT} + \left(\frac{\partial p}{\partial T}\right)_{x_{13}},$$

from which follows:

$$\left(\frac{\partial p}{\partial T}\right)_{x_{23}} - \left(\frac{\partial p}{\partial T}\right)_{x_{13}} = \frac{dx_3}{dT}\left\{\left(\frac{\partial p}{\partial x}\right)_{13} - \left(\frac{\partial p}{\partial x}\right)_{23}\right\},$$

not only the sign, but also the value of the abrupt change of direction in the course of the upper branch is determined. But this modification remains restricted between the two indicated temperatures — and neither of the lower sheet nor of the remaining part of the upper sheet does the shape change in any respect. Only the lower sheet undergoes some modification, but in sections of quite different values of x, namely those which are found between the values of x of the points Q'_1 and Q'_2. And this modification occurs only for one single value of T, at least so long as the curve $Q'_1 Q'_2$ has the property of being cut only once by a line normal to the x-axis.

The modification in the course of the lower branch consists in this that for certain value of T, to be derived from the curve $Q'_1 Q'_2$, the lower branch begins to rise less steeply. The three-phase-pressure ascends then even more rapidly than the first direction of the lower branch did. Below the temperature at which this change in the course of the lower branch appears, the three-phase-pressure is already found, but for the considered section it may be considered only as a parasitic branch. The part of the three-phase-pressure that belongs to higher temperatures lies and terminates in the unstable region, i.e. above the lower sheet of the surface of saturation. At least if $Q'_1 Q'_2$ is not intersected for the second time at the same value of x. In this case a second, higher temperature occurs, for which the three-phase-curve runs below the lower sheet, and again a part of this curve becomes a parasitic part. But for all the sections between Q'_1 and Q'_2 the upper sheet is not subjected to any change. The proof of what was said here about the modification of the lower sheet, is again found in the equations, which now with change of the indices, assume the form:

$$\frac{dp}{dT_{123}} = \left(\frac{\partial p}{\partial x}\right)_{21} \frac{dx_1}{dT} + \left(\frac{\partial p}{\partial T}\right)_{x_{21}},$$

and

$$\frac{dp}{dT_{123}} = \left(\frac{\partial p}{\partial x}\right)_{31} \frac{dx_1}{dT} + \left(\frac{\partial p}{dT}\right)_{x_{31}}.$$

If, as is the case on the curve $Q'_1 Q'_2$ the three-phase-pressure comes inside the heterogeneous region with ascending temperature then $\frac{dp}{dT_{123}} > \left(\frac{\partial p}{\partial T}\right)_x$, and $\left(\frac{\partial p}{\partial x}\right)_T$ being negative on the whole lower sheet now that the second component is assumed to have higher T_k than the first component, $\frac{dx_1}{dT}$ is necessarily negative, as was drawn for the curve $Q'_1 Q'_2$. But as we see from the properties of a p,x or

v,x-section of the surface of saturation at given temperature, $\left(\frac{\partial p}{dx}\right)_{31}$ is in absolute value greater than $\left(\frac{\partial p}{\partial x}\right)_{21}$. Hence $\frac{dp}{dT_{123}} - \left(\frac{\partial p}{\partial T}\right)_{x_{31}}$ is greater than $\frac{dp}{dT_{123}} - \left(\frac{\partial p}{\partial T}\right)_{x_{21}}$.

So the section of the surface that holds for the equilibrium 3,1 ascends less rapidly than the section 1 for the equilibrium 2,1. And in consequence of the retrogression of x to smaller value at rising temperature the sheet 3,1 comes in the place of the sheet 2,1. If at a second, higher temperature the three-phase-curve should again leave the heterogeneous region, and become a parasitic line below the lower sheet, then $\frac{dp}{dT_{123}} < \left(\frac{\partial p}{\partial T}\right)_{x}$. Hence the value of $\frac{dx_1}{dT}$ is positive, because $\left(\frac{\partial p}{\partial x}\right)_{T}$ continues to be negative. Then both $\frac{dp}{dT_{123}} - \left(\frac{\partial p}{dT}\right)_{x_{31}}$ and $\frac{dp}{dT_{123}} - \left(\frac{\partial p}{\partial T}\right)_{x_{31}}$ are negative; but the first difference is greater in absolute value than the second. So $\left(\frac{\partial p}{\partial T}\right)_{x_{21}}$ is then smaller than $\left(\frac{\partial p}{\partial T}\right)_{x_{31}}$. There is then another break in the section of the lower sheet, but yet in consequence of this this section begins to ascend less rapidly, because on account of x_1 running to the right with rising temperature the sheet 2,1 takes the place of the sheet 3,1.

But though it is good that these circumstances have been examined in detail, all this is not necessary if we only want to know what will be the shape of the line at higher temperatures with regard to that at lower temperatures, if a break appears in the lower branch. The simple remark that the two branches which meet, must have such a position with respect to each other that their continuations representing metastable branches may not lie in the stable homogeneous region, is then sufficient, and evidently this rule could not be satisfied if on the lower branch the line occurring at higher temperatures ascended more rapidly than the preceding one. But for the upper branch this rule leads to the conclusion that on the contrary a branch appearing at higher temperatures, must ascend more rapidly.

The systematically sustained application of this rule, therefore, does not present any difficulty in the case of fig. 40, and does not reveal anything new so long as P_{ab} lies higher than A, as in the case with the mixtures of ethane and alcohols. But in the cases of BUCHNER, mixtures of CO_2 and organic liquids where P_{ab} lies lower than T_{k_1}, it will have to give rise to what we may call: double retrograde condensation. So long, namely, as P_{ab} continues to lie higher than T_{k_1} the three-phase-line $Q_1 Q_2 Q'_1 Q_2'$ can lie entirely on the upper sheet of the surface of saturation, and can then give only rise to the more rapid ascent of the upper branches of the sections at given value of x. Above the temperatures at which this more rapid rise sets in, the section has then its usual shape, merging continuously into the vapour branch, there being only one point where the tangent is normal to the T,x-plane. The temperature at which the upper branch suddenly begins to rise more rapidly is given for every section by the value of T for the points of the dotted curve, which, however, must then be broken off before the point with minimum value of x. Sections on the right side of Q_2' and the left side of Q_2' present the wholly unmodified shape. Sections between Q_2' and Q_1 get the break in the upper sheet at ever lower temperature as the point Q_1' is approached. In each of these sections part of the line of intersection with the three-phase-sheet, i. e. a part that belongs to lower temperatures lies above the upper branch. The higher part of this line of intersection lies and terminates in the heterogeneous region. For the section of Q_1 this line of intersection lies over its full length in this region, and the initial direction at Q_1 then touches the upper branch of the section of Q_1, as it proceeds unmodified at lower temperatures. For sections between Q_1 and Q_2 the point of intersection of the upper sheet with the three-phase-line lies at ever higher temperatures as we approach Q_2. The lower part of the three-phase-line then lies below this upper branch, and the upper part would project above it; but the abrupt change of direction taking place at the intersection is so great that even the upper part of the three-phase-line remains in the heterogeneous region. So if we want to keep a section between Q_1 and Q_2 in homogeneous liquid state, the pressure must always be greater than the three-phase-pressure with the exception of the liquid represented by the point of intersection. For the section of Q_2 the three-phase-line lies entirely in the unmodified heterogeneous region, and in the highest point it touches the upper branch. For the sections on the left of Q_2 the upper part of the three-phase-line lies again above the upper branch, and as such it has lost its significance. Then these sections, too, have the sudden change of direction, at which they begin to ascend more rapidly, but at ever lower temperature the more we go to the left. For the section of the point Q'_1 the whole of the three-phase-line lies then above the upper sheet.

So when the three-phase-line over its full width intersects only the upper sheet, there is no further complication; and this may be the case if $P_{ab} > T_{k_1}$. Also in this case, however, the possibility remains that on the lefthand side the intersection takes place in points of the lower sheet. But the latter must take place if $P_{ab} > T_{k_1}$. And in the transition of the point of intersection of the upper sheet to the lower sheet we meet with the complication which I am now going to discuss, but which will perhaps be easier to understand, when I shall discuss the properties of the *p,x*-sections of the surface of saturation, so sections at constant temperature.

If we think such a *p,x*-section at a temperature only little lower than T_{k_1}, the upper branch has, leaving the line of the equilibrium between the two liquids out of consideration, the known shape with a minimum and a maximum between x_2 and x_3, because the three-phase-pressure exists, P_{ab} being $< T_{k_1}$. The third phase then lies on the lower branch at $x_1 < x_2 < x_3$, and if at higher temperatures $\frac{dp}{dT_{123}} < \left(\frac{\partial p}{\partial T}\right)_{x_1}$, the value of $\frac{dx_1}{dT}$ is then already positive. At a temperature somewhat above T_{k_1} the *p,x*-curve has got detached from the axis ($x = 0$), and has a point where $\frac{dp}{dx} = \infty$, and so $v_{21} = 0$. But then the point 1 still lies on the lower sheet. Now we might suppose and I have held this opinion myself, and I think I have given diagrams in accordance with this view, that on further rise of the temperature the critical point of contact for the equilibrium 2,1, would proceed so far towards greater value of x_1 that it would coincide with the coexisting vapour phase, but that then at the same time this third coexisting phase would be critical point of contact for the equilibrium 3,1, to render it possible for the metastable branches to be contained in the heterogeneous region. If this were possible the third phase would have come on the upper sheet at still higher temperature — and in this case there would be no question of complication. But that this concurrence of circumstances cannot take place we see when we examine its signification. First of all I observe that we cannot put that $v_{21} = 0$ coincides with $v_{31} = 0$ without proof, and that "else we get other complications" cannot be accepted as a proof. But we may also directly see that $v_{21} = 0$ cannot exist in the same point as $v_{31} = 0$. Then $\frac{v_2 - v_1}{x_2 - x_1} - \left(\frac{dv_1}{dx_1}\right)_{pT} = 0$ would have to hold, and at the same point also $\frac{v_3 - v_1}{x_3 - x_1} - \left(\frac{dv_1}{dx_1}\right)_{pT} = 0$. Or the tangent to the isobar in the point x_1 would have to pass both through the point x_2 and through the point x_3, and this isobar would have to be at the same time the isobar of these two latter points, and the three points

1, 2 and 3 would have to lie in a straight line in the x,v-diagram. If we follow the course of the isobar separately for the condition $v_{21}=0$, the possibility for this condition to be satisfied at temperatures above T_k follows at once. In the same way separately for the condition $v_{31}=0$. But for these two conditions to be fulfilled simultaneously the isobars would again have to possess points of inflection, which we should certainly have to consider as quite abnormal cases. But there is more. Then $\frac{dp}{dT}_{123}$ would have to be $=\infty$, for the denominator is then equal to zero; and if we wish to avoid this, we should have to make again an entirely arbitrary supposition, viz. that then also $\frac{\eta_2-\eta_1}{x_2-x_1}$ would be $=\frac{\eta_3-\eta_1}{x_3-x_1}$. Therefore I do not hesitate to reject the thesis that $v_{21}=0$ coincides with $v_{31}=0$ as entirely erroneous. Then there remains no other possibility than to assume that the sheet of equilibrium 2,1 when contracting with rising temperature, passes through the critical point of contact of the sheet of equilibrium 3,1, before having got hidden under this sheet. Then the third phase passes from the lower part to the upper part of the sheet 3,1. But this implies that at still somewhat higher temperature for a value of x which is somewhat higher than that of the critical point of contact of 3,1 a vertical line can intersect the whole sheet of saturation 4 times. And if the circumstances are chosen in such a way that the chosen value of x is also smaller than that of the plaitpoint of the equilibrium 2,1, retrograde condensation must occur twice.

In fig. 41^a I have drawn the p,x-line in the neighbourhood of T_{k_1} schematically. The discontinuity in the two vapour branches intersecting each other in the point 1 is such that the branch which belongs to the equilibrium 3,1 descends more rapidly than that which belongs to the equilibrium 2,1.

Now $\left(\frac{dp}{dx_1}\right)_{31}=\frac{\left(\frac{d^2\zeta}{dx_1^2}\right)_{pT}}{\frac{v_{31}}{x_3-x}}$, and also $\left(\frac{dp}{dx_1}\right)_{21}=\frac{\left(\frac{d^2\zeta}{dx_1^2}\right)_{pT}}{\frac{v_{21}}{x_2-x_1}}$.

If $\frac{v_{31}}{x_3-x_1}$ has become 0, $\left(\frac{dp}{dx_1}\right)_{31}$ has got equal to $-\infty$, and $\left(\frac{dp}{dx_2}\right)_{31}$ has then a large negative value. Or in other words if $v_{31}=0$, v_{21} has still negative value, though it be a small one. But then it is exactly this that follows from the known course of the

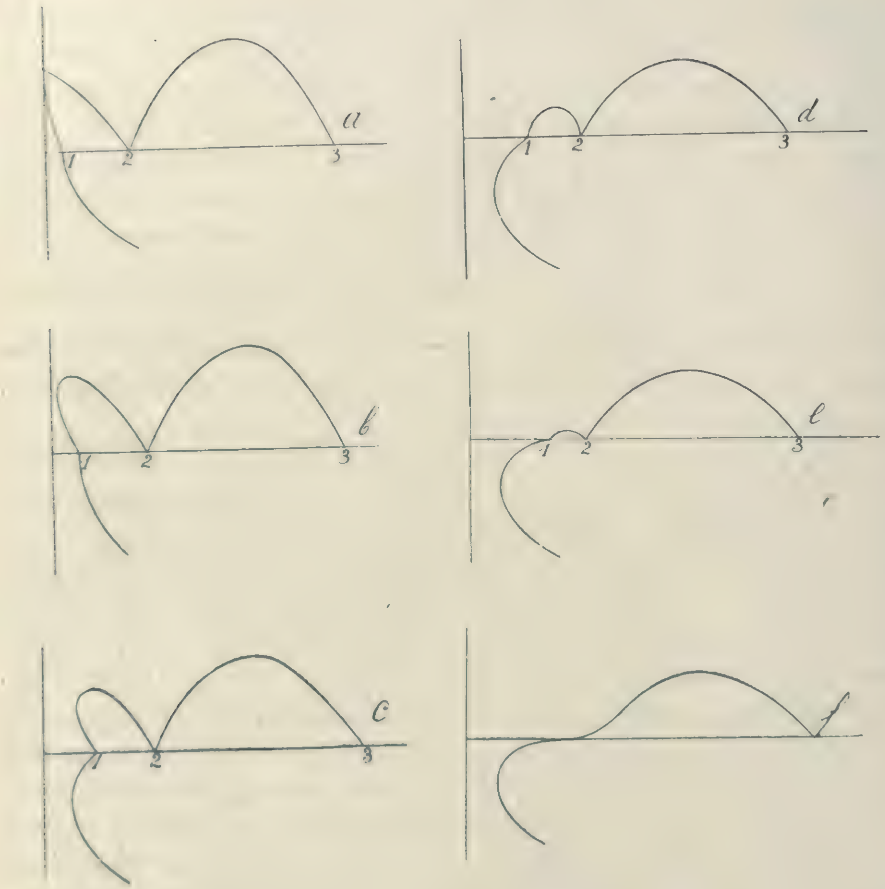

Fig. 41.

isobars. The isobar which passes through the point 3, has its convex side turned towards the v-axis in this point, has a point of inflection in its course to the point 1, and touches the line joining the points 3 and 1 in this point. But then the point 2 lies in such a way that:

$$\frac{v_{21}}{x_2-x_1}=\frac{v_2-v_1}{x_2-x_1}-\left(\frac{dv_1}{dx_1}\right)_{pT}=\frac{v_2-v_1}{x_2-x_1}-\frac{v_3-v_1}{x_3-x_1}$$

is negative. In fig. 41^b the p,x-line is drawn for the temperature for which this is the case. At again a somewhat higher temperature the p,x-line has the shape of fig. 41^c. Then mixtures for which the value $x < x_1$ can show the double retrograde condensation. A favourable, if not the most favourable case occurs if the points for which $v_{31} = 0$ and $v_{21} = 0$, lie in the same line normal to the x-axis. At somewhat higher temperature, i. e. when the p,x-line has the position of fig. 41^d, the opportunity is past. Then $v_{21} = 0$, and

$\frac{v_{31}}{x_3-x_1}-\left(\frac{dv_1}{dx_1}\right)_{pT}=\frac{v_3-v_1}{x_3-x_1}-\frac{v_2-v_1}{x_2-x_1}$ is then positive. So the denominator of $\frac{dp}{dT_{123}}$ has always the same sign, and does not pass through zero. But now that $\frac{v_{31}}{x_3-x_1}$ is positive, $\left(\frac{dp}{dx_1}\right)_{31}$ has also become positive. The figs. 41^e and 41^f do not call for further elucidation.

Whether the experiment will succeed in showing this double retrograde condensation, the investigation will have to prove. The fact that it only undoubtedly exists for such small values of x which do not only lie below x_1 but must moreover be smaller than the value of x of the plaitpoint of the equilibrium 2,1, and the circumstance that for such small differences in the value of x the condensed part is exceedingly slight, will certainly impede the observation greatly. Moreover we shall have to find cases in which the occurrence of the solid state is no impediment. We might begin to try and show that after the termination of the first retrograde condensation of the equilibrium 3,1 another condensation makes its appearance with further raised pressure. The very appearance of this new condensation after the first is finished, might be considered as a not unimportant addition to our knowledge of the complex phenomena of not perfectly miscible binary mixtures. And it must be called surprising that if the possibility of splitting up into two phases differing so much in concentration as the states 1 and 3 is past, at still higher pressure the possibility of splitting up reappears for phases differing as little as the states 1 and 2. A value of $n=4$ and $\frac{pk_2}{pk_1}=\frac{1}{2}$ might be serviceable.

To attain these results we might also have made use of the properties of the p,T sections of the surface of saturation; and it is even by the consistent application of the rules for the change in direction when such a p,T-section is intersected by the three-phase-sheet that I have arrived at these results. The complication only occurring in sections on the left of Q_2, we shall confine ourselves to the discussion of these sections in what follows. Thus at a value of x somewhat smaller than that of Q_2 the upper branch will be cut by the three-phase-curve, and that at a temperature somewhat higher than that of the plaitpoint of this section. In such a point $\left(\frac{\partial p}{\partial T}\right)_x$ is either small, or perhaps already negative. But whatever may be the value of this quantity, the upper branch will suddenly change its direction at the temperature of the intersection with the line p_{123}, and that in such a way that $\left(\frac{\partial p}{\partial T}\right)_x$ is greater after the intersection than before the intersection. If $\left(\frac{\partial p}{\partial T}\right)_x$ should be equal to zero before the intersection, this quantity is again positive after the intersection. If it should be negative for a section of still smaller value of x, it is negative but smaller in absolute value or perhaps even positive after the intersection. If the intersection should take place in the critical point of contact, and so $\left(\frac{\partial p}{\partial T}\right)_x$ be $-\infty$, so that the whole of the upper branch has been entirely completed when the break appears, then — and the properties of the following sections depend on the conclusion at which we arrive — the following direction either coincides with the preceding one, so that $\left(\frac{\partial p}{\partial T}\right)_x$ remains $= -\infty$, or it is negative. Now the former supposition is excluded, for it requires that in the same point $v_{21} = 0$ and $v_{31} = 0$. But for following sections the point of intersection with the three-phase-line must then lie on the lower branch of the sheet 2,1 and on the upper branch of the sheet 3,1. This continues till the value of $\left(\frac{\partial}{\partial T}\right)_{x_{31}} = \infty$ in the point of intersection. So there are sections for which a line normal to the T,x-plane can intersect the surface of saturation 4 times.

If fig. 42 I have drawn the quantity $T - T_{k_1}$ as function of x on a large scale for the plaitpoint line, for $v_{21} = 0$ (the point of contact line for the equilibrium 2,1), for $v_{31} = 0$ (the point of contact line for the equilibrium 3,1), and for the vapour phase of the three-phase-curve. Only for the value of x contained between the points in which $v_{21} = 0$ and $v_{31} = 0$ intersects the dotted curve (vapour phase), the discussed phenomenon occurs.

Where the curves $v_{21} = 0$ and $v_{31} = 0$ intersect the value of x is the same, but the value of the pressure is different for the value of $T - T_{k_1}$ belonging to the point of intersection. For $v_{21} = 0$, p is larger than for $v_{31} = 0$. And this is in perfect harmony with what is known of the course of the isobars, which I shall set forth at some length. As the line $\frac{dp}{dv} = 0$, because we are dealing with temperatures above T_{k_1}, is closed in a critical point, there is a locus for the points of inflection of the isobars which passes through this critical point, and speaking roughly, about coincides with the critical points of the mixtures with smaller value of x. If we now think successive isobars drawn, starting with that of the point in which $\frac{dp}{dv}=0$ is closed, they all have their points of inflection at ever

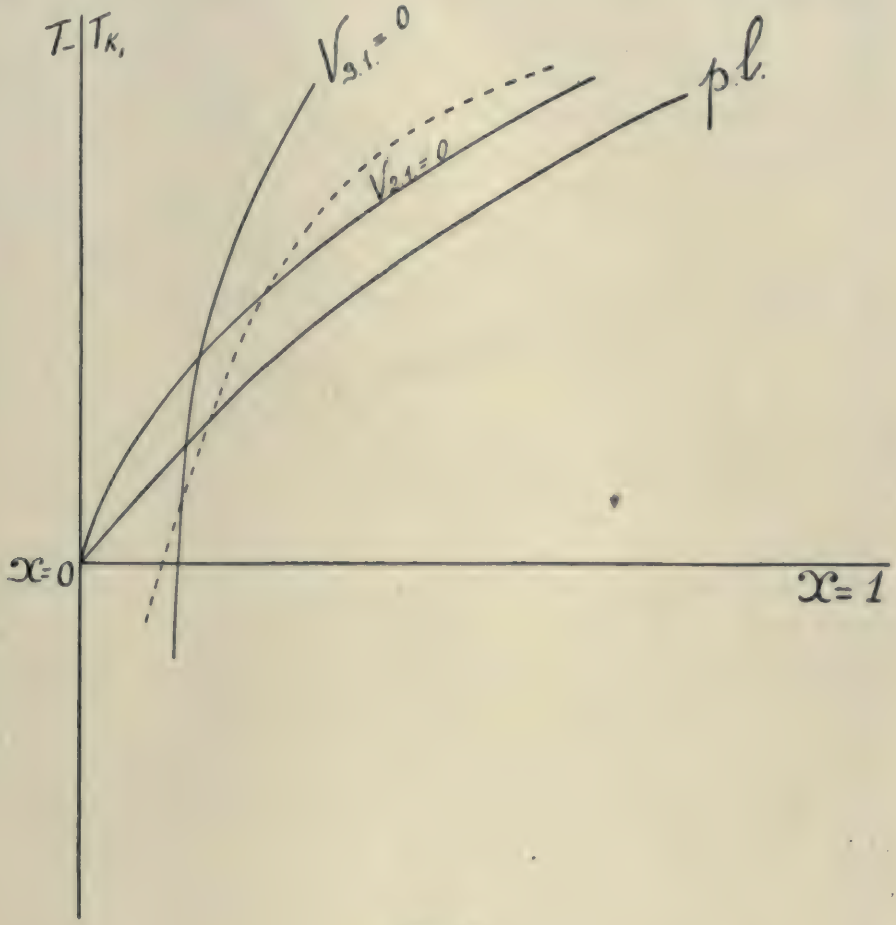

Fig. 42.

smaller value of x. If we now take the point in which $v_{31}=0$, and if we draw the isobar of this point, and the tangent to this isobar, this tangent must pass through the point 3, which is only possible when the point of inflection lies between 1 and 3. If we then take the point in which $v_{21}=0$, so on a higher isobar, and if we again draw a tangent to that higher isobar in that point, this tangent will point at a point 2 which lies nearer 1 than 3 lies near it, the point of contact now being nearer the point of inflection.

It appears from the diagram of the considered case that the three-phase-pressure is always smaller than the vapour tension of the first component at the same temperature. Observations, however, have repeatedly been made which would on the contrary give a greater value for the three-phase-pressure. If this result is real, and not the consequence of errors of observation, the circumstances must be different from those supposed above. Accordingly I have tried if it could be possible to account for such a phenomenon. If we think three-phase-pressure also possible for a system with minimum value of T_k, p_{123} must really always be larger than the vapour tension of each of the components at the same temperature. And though objections might be advanced against this possibility which I do not consider as entirely devoid of importance, I have set these objections aside, and examined what would be then the further circumstances of the course of the three-phase-pressure.

The first representation of the ψ-surface, which I gave already in my Théorie moléculaire etc., supposed this possibility, and in figure 11 of these contributions I have expressly pointed it out. I will, however, immediately state that then the highest temperature at which three-phase-pressure is still possible, must lie below T_{k_1}.

At lower temperature the p,x-figure consists of two branches which start from p_1 and point upward. In the same way of two branches starting from p_2, in which p_2 must be thought much smaller than p_1. At the point where the two vapour branches intersect, the coexisting vapour phase is found. Let us again call the concentration of this phase x_1. An horizontal line drawn through this point of intersection, contains the points which represent the two coexisting liquid phases with concentrations x_2 and x_3. Then we have $x_2 < x_1 < x_3$. Let us complete this figure by tracing the rapidly ascending line for the equilibrium 2,3. We always have then $\frac{v_{12}}{x_1-x_2} > \frac{v_{32}}{x_3-x_2}$.

With rise of temperature the branches starting from p_1 contract, and close to T_{k_1} they must have almost entirely retracted into the axis $x=0$, and so have got clear from the other part of the p,x-figure. So there is a temperature and that below T_{k_1}, at which the three-phase-pressure has vanished. What has been left on the right, is a continuous curve for the equilibrium 3,2. If we examine the circumstances occurring when the branches get detached more in details, we observe that if the line for the equilibrium 2,3 is vertical, and so $v_{32}=0$, $\frac{v_{12}}{x_1-x_2}$ is positive, and hence $\left(\frac{dp}{dx_2}\right)_{12}$ is positive. Where the curve retracting into the x-axis, is vertical, the value of $\frac{dp}{dx}$ is negative for the equilibrium 2,3. And when the two points 2 and 1 coincide, there is again a point where $\frac{dp}{dx} = 0$ and $\frac{d^2p}{dx^2} = 0$ in the righthand part, but in contrast to what took place before this point now lies on the lower branch. At a temperature somewhat higher than that of the branches getting detached, there are now again values of x, for which a line normal to the x-axis has four points of intersection in common with the two detached branches. At lower pressure we then meet with phenomena of condensation for the equilibrium 1,2 and at higher pressure for the equilibrium 3,2. Then there is homogeneity between these pressures.

If we also inquire into the course of the T,x-projection of the plaitpoint line and the three-phase-line in this case, a difference can immediately be pointed out compared with fig. 40 that on the left side the vapour branch does not belong to smaller but to greater value of x than the liquid branch. I have drawn a schematical representation of the two lines in fig. 43, assuming that the three-phase-pressure does not continue to exist as far as $T = 0$. The full line which begins in A, descends to Q_2, rises again to P_{cd}, then descends to P_{ab}, after which it rises to the critical point of the second component, is the plaitpoint line. So compared with fig. 40 the ascending part AP_{cd} of this figure has still a minimum, and further it has been considered as possible that the descending branch of this figure has a maximum and a minimum value of x. The part AQ_2 contains the realisable plaitpoints of the branch which retracts into the x-axis, after it has got detached from the righthand part of the p,x-lines. At the temperature indicated by Q_2 the two parts join, which, however, may not be called contact. Then the spinodal curves and the binodal curves intersect in one point, whereas above T_{Q_2} these lines remain at a distance from each other. So here the same circumstance is met with which occurs for mixtures with minimum T_k, but for another value of T and x. With rise of the temperature from below T_{Q_2} to above it two realisable plaitpoints appear. One of them was mentioned before, but the other lies in the considerably larger righthand part. Though we have called it realisable, it does not show itself but remains covered under the more stable equilibrium 3.2. If phenomena of retardation could appear, it would be realisable — a circumstance which always occurs if splitting up of the spinodal line takes place for three-phase-equilibria. These plaitpoints lie on the branch Q_2P_{cd}.

For the discussion of the remaining part of the plaitpoint line we shall begin with P_{ab}. At the temperature of this point an heterogeneous double plaitpoint arises and with rising temperature these plait-

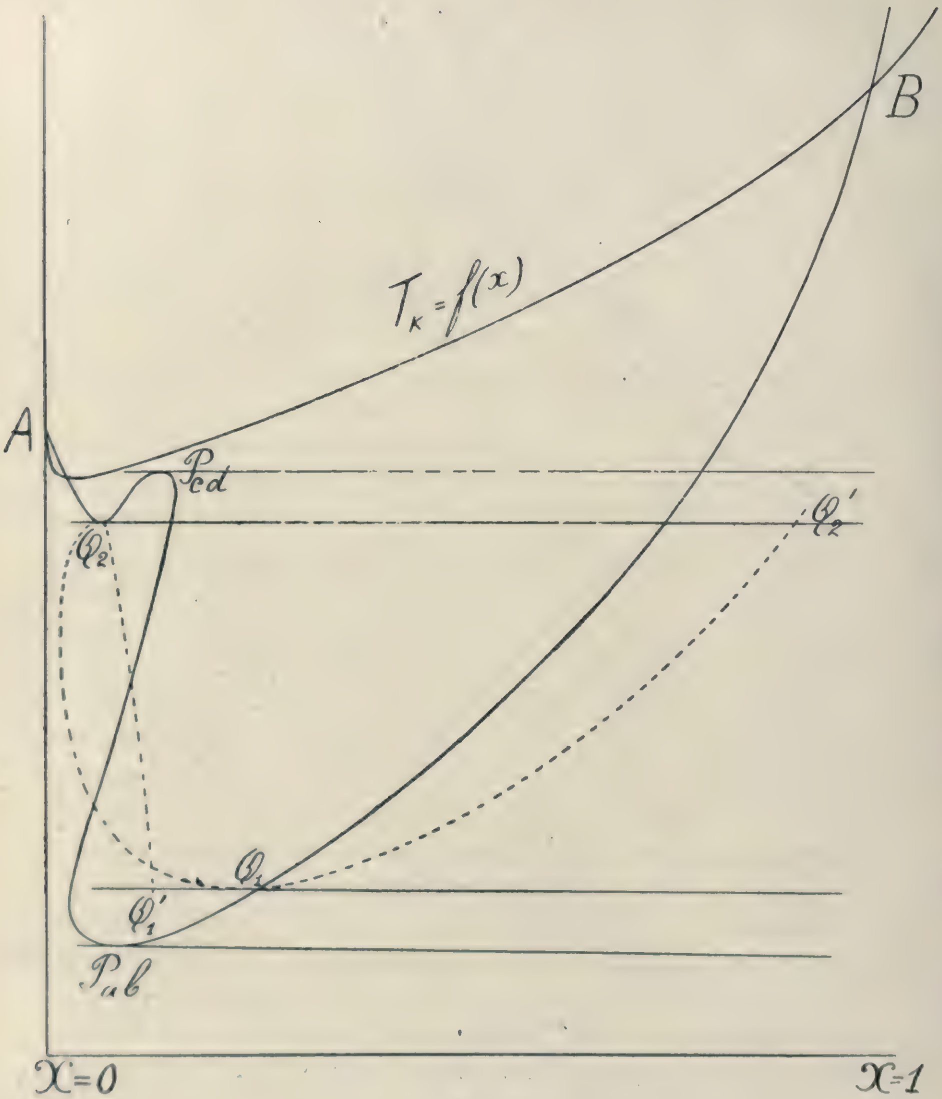

Fig 43.

points get further apart. This yields the branch which runs upward on the right of P_{ab} and terminates in the critical point of the second component, and the lefthand branch which contains the hidden plaitpoint. At first we can consider this hidden plaitpoint as belonging to the realisable part of the righthand branch, till the temperature is reached at which occurs what I have called: "Transformation of of a branch plait into a main plait and vice versa" (These Proc. March 25 p. 621). Now at the beginning and long after, the liquid sheet 2,3 is the branch plait, and then a hidden plaitpoint always belongs to the plaitpoint which lies at the top of this sheet. But at temperatures which draw near to T_{k_1} the equilibrium 2,3 will have become the main plait, and the sheet 2,1 must be considered as a branch plait and then the hidden plaitpoint belongs to this sheet, and the plaitpoint lying on the branch $Q_2 P_c$ and the hidden plaitpoint form together a pair.

So at the temperature of the splitting up of the spinodal line the points forming this pair must still be a certain distance apart. At higher temperature, in the drawing at T of P_{cd}, they coincide. A consequence of this transformation of the lefthand part to a branch plait, and reversely of the righthand part to a main plait is among other things that at higher temperatures on the lefthand side the metastable and the unstable branch of 2,3 form a line which proceeds continuously, with a minimum pressure on the side of 2, and a maximum pressure on the side of 1, whereas these branches have for the equilibrium 2,1 the intricate shape known of a branch plait, and on which a hidden plaitpoint then occurs.

The three-phase-pressure is represented by the dotted line $Q_1'Q_2Q_1Q_2'$ in fig. 43. The branch $Q_1'Q_2$ is the vapour branch. With regard to some particulars, a difference must be made depending on whether the 1st component, viz. that for which $T_{k_1} < T_{k_2}$, has also the smallest value of b. But as far as these and other particulars are concerned, it is perhaps better to wait if direct experimental investigation yields data for this.

With regard to the p,x-projection of the plaitpoint line and the three-phase-line it suffices to state that if $\frac{dT}{dx} = 0$, also $\frac{dP}{dx} = 0$. While moreover a maximum for P_{pl} can occur on the side of the 2nd component, if $\frac{dP_{pl}}{dT} = 0$.

And now in conclusion this remark. If the three-phase-pressure begins above T_{k_1}, it depends on the following circumstance whether double retrograde condensation occurs or not. Let us think the well-known looplike p,x-curve drawn at T_{Q_1}. If now the three-phase-pressure appears on the upper sheet in a point that lies lower than the critical point of contact, it must occur at higher temperature. In the other case not.

Physics. — "*New methods of stereoscopy*". By Dr. P. H. EYKMAN. (Communicated by Prof. K. F. WENCKEBACH).

In a paper of mine, which was recently published, entitled: "stereo-Röntgenography" (Nederl. Tijdschr. voor Geneeskunde, March 13, 1909), I pointed out that from a mathematical point of view stereoscopy by means of the Röntgen rays is much simpler than ordinary stereoscopy by means of a photographic camera with lenses. With Röntgen rays both the object and its projection are on the same side of the centre of projection, whereas with the camera they lie one on either side of the centre of projection and moreover the image is reversed. With the camera owing to the relative position of the conjugate foci the ratio of the distances is fixed. With the Röntgen rays this is not the case. With the camera the photographic plate must be perpendicular to the principal axis, otherwise the image will be hazy in parts. With the Röntgen rays the plate may be at any angle, but I have only considered the "normal case", so as to simplify the construction. I pointed out the mistake of applying the laws of lens-stereoscopy to Röntgen-stereoscopy, whereas in my opinion the better way is to derive ordinary stereoscopy from Röntgen-stereoscopy. The so-called "pinhole-camera" is a transition between the two, as in this case the law of conjugate foci does not apply, and there is no principal axis. VAN ALBADA understood this, and when treating the theory of stereoscopy, placed the object and the picture on the same side of the centre of projection, e.g. the observer looking out of a window, the window-pane representing the plane of projection. For the mathematical reconstruction, the two Röntgen plates or their virtual images must be superimposed exactly at the same spot, and in the same position with regard to the two anticathodes. Further since the anticathodes must be replaced by the eyes, the distance between the two anticathodes (base of exposure) must be equal to the distance of the optical centres of the two eyes (visual-base). In practice this distance may be fixed at 65 millimeters.

The following conditions are requisite for the normal stereoscopic exposure:

1. In the two exposures one plate must be placed exactly in the same place as the other, in other words, the plates must be congruent.

2. The base of exposure must be 65 millimeters.

3. The nearest point of the object must be at least 25 centimeters from the anticathode, since at a lesser distance the eyes do not see stereoscopically.

4. The base must be parallel to the photographic plate, the middle

point of the base being opposite the middle of the plate. We may call the perpendiculars from the extremities of the base the principal axes, and their intersections with the plate the foot-points.

All other cases may be considered as deviations from the normal exposure and may be easily derived therefrom.

For the mathematical reconstruction the mirror-stereoscope is the best. The double mirror-stereoscope after the model of the HELMHOLTZ telestereoscope is to be preferred, since with this instrument the illumination of the plates is the most equable.

When viewing the reduced pictures of the original negatives, a lens stereoscope is best, fitted with plan-convex lenses of 10 Dioptries. This is to be recommended, because simple formulae are obtained for the mathematical reconstruction. From these formulae, which I have already given, it ensues that there exists a simple connection between the length of the principal axis (exposing-distance) and the number of times the original image must be diminished. If for instance the exposure has been made with the normal base, the number of times the picture is to be diminished is exactly one more than the length of the exposing-distance expressed in decimeters. Thus with an exposing-distance of 5 decimeters the size of the original exposure negative is reduced to $\frac{1}{6}$. From the degree of diminution we can calculate the distance there must be between the image and the lens.

For convenience' sake I have always spoken of the left half-image as belonging to the left eye, and the right half-image to the right eye. Properly speaking however this applies only to landscape-photography, since we never require to view a landscape upside down. With ordinary objects however, and this applies both to common light as well as the Röntgen rays, it is often of advantage to view an object upside down. This is easily accomplished with a lens-sterescope by simply turning round the plate on which the two half-images are impressed, so that the so-called left half-image is placed in front of the right eye and the right half-image in front of the left eye. The same thing of course occurs with the original plates, if they are turned round in the same manner. Mathematically speaking, the image is not altered by turning it upside down. Psychically however this is not necessarily the case, and in some cases this distinction may be of importance. In what follows I shall regard the matter exclusively from a mathematical stand-point, the two half-images being considered as a single stereo-image.

I. *Polyphany.*

The images we have to consider are central projections. The connection between the two stereoscopic half-images is expressed by the fact that the exposing-distance is the same for both, the centres of the two projections being separated by a definite distance which we call the base length. It will be readily understood that we may make any number of half-images, from any number of points which satisfy these requirements. Any given half-image is not limited to only one corresponding half-image, but the number is unlimited. The question thus arises, whether it may not be of advantage in practice, to make a stereoscopic exposure from more than two points. A simple experiment will answer this question in the affirmative.

If we hold a cylindrical stick in a horizontal position at a short distance before the eyes, both eyes receive one and the same image of the stick and that what is hidden behind the stick from one eye, is also hidden from the other eye.

It is quite different however, if we hold the stick in a vertical position, for then the left eye sees behind the stick what is hidden from the right eye, and the right eye sees what is hidden from the left. A similar phenomenon may be observed with the Röntgen rays. If in taking a skiagram of any object we place a thick wire parallel to the base, there will be no representation on either plate of what is situated before or behind the wire. Hence it is impossible to decide whether this wire is placed before or behind the object. If however we place the wire perpendicular to the former direction, one is able to see with perfect clearness, at what depth the wire is situated.

Figure I shows a skeleton hand, in which the fingers are placed in a very unnatural position. Four exposures have been made, the respective projection-centres making a square of 65 millimeters in a plane parallel to the plate. Under the hand in a transverse direction is a metal staff. Holding the plate so that the fingers point upwards and examining the two lower images through the stereoscope, one cannot distinguish whether the metal staff is behind or in front of the hand.

Likewise if we look at the two uppermost pictures, one is also in doubt as to the position of the metal staff. Mathematically speaking we has obtained all the information derivable from these four pictures. Psychically speaking however this is not the case. When we turn the plate on its side and examine the upper pair of pictures by the stereoscope, we obtain at once an accurate impression of the position of the metal staff. We may in the same way examine the other pair, with a like result, and we shall find that other details such as the shape of the fingers, are also shown much more clearly. In my opinion such series of four skiagrams, which may be viewed two by two in various ways, has a decided advantage over the usual pair of stereographic pictures. I have given the name "Tetraphany" to this method.

The result is almost as good if we make three such negatives as in Figure 3 with the centres of projection at the angles of an equilateral triangle (Triphany). In practice a threefold exposure will probably be sufficient. Having regard to the usual oblong shape of the photographic plate, it is advisable to place the foot-points of the principal axes in the position shown in Figure 4.

It may in special cases be advantageous to place the three anticathodes in a straight line instead of a triangle. We may thus obtain a stereoscopic view of any two of the negatives. The outer pair give a stereo-image of half size and at half the original distance.

With the ordinary mirror-stereoscope, the breadth of the plate should not be more than the distance of exposure, whereas the length of the plate is not limited. In Tetraphany (in the form of a square) the length as well as the breadth of the plate is limited by the exposure-distance.

In Triphany (equilateral triangle) the mirror-stereoscope may easily be adopted for viewing the negatives. A third set of mirrors is added, so that each pair of images may be examined without having to interchange the plates. If the exposure has been made according to figure 4, the length of the plate must not exceed the exposing-distance, whereas the breadth must not exceed $\frac{1}{2}\sqrt{3}$ of the exposing-distance. (This number is the ratio of the vertical to the sides of an equilateral triangle, i. e 56 : 65).

For the examination of the images it is simplest to have a lens-stereoscope with three lenses, the centres of which make an equilateral triangle having sides of 65 millimeters.

The principle of Polyphany which I have thus described for Röntgenography, may also be made use of for any other variety of stereoscopy.

II. *Symphany.*

In drawing the mathematical reconstruction of a mirror-stereoscope, the virtual images must coincide with the original position of the negatives. The stereo-image appears on the exact spot where the object lay of the same size and in the same place, so that we may say that the stereo-image is congruent with the original object. Figure 5 is a representation of the course of the rays in the double mirror-stereoscope corresponding to the HELMHOLTZ telestereoscope. It is evident that the eyes at L and R are unable to see the object lying before the plate P, firstly because the small mirrors S^1_l and S^1_r are opaque and secondly because the photographic plates P_l and P_r obstruct the view. The first difficulty may be obviated by using semi-transparent mirrors of thin plate-glass. The second difficulty may be obviated by making the plates somewhat narrower, or placing them farther apart. By this means we are able to see at the same time the original object and the stereo-image on the same spot. In the human body one may see the bones through the skin in their exact relative position. This may serve as a guide to the surgeon during an operation, since he is able with mathematical accuracy to apply his scalpel to the actual spot. The course of the rays is represented in fig. 6. The great drawback for the surgeon from a practical point of view is that the two plates P_r and P_l impede the field of operation. This may be easily remedied however, for the mirror-stereoscope admits of all sorts of variations. For instance in fig. 7 the negatives are situated above the observer instead of below, and at such a distance apart as not to interfere with the surgeon's head. This has another advantage in that the photographic plates lie horizontally above the surgeon and are therefore well lit up since the operating-theatre is as a rule lighted from above. It depends merely upon the degree of illumination, whether the Röntgen-image is more visible than the part to be operated upon, or whether the reverse is the case. The degree of illumination may easily be regulated, by diminishing the transparency of the small mirrors by a screen of smoked glass, enhancing the relative clearness of the Röntgen stereo-image. This method, i. e. the contemporaneous presence of the object itself together with its Röntgen-image may be termed *Symphany*.

An important province of Röntgenology is stereogrammetry, the measurement of the depth of a foreign body. For this purpose I have designed an instrument which I may call the *Symphanor*, fig. 7. Let us suppose, that we cannot get at the object itself but that in its stead we have the virtual stereo-image. We may place a divided rule across any diameter of this virtual stereo-image, and thus measure the exact distance between any two points. This method I call *Symphanometry*, a method, which should prove of use for the record of scientific measurement as for instance in craniometry, if we have a pair of stereoscopic skiagrams of a cranium we may measure the diameter of the stereo-image in various directions by means of the symphanator. We thus possess in the stereogram a means not only of reproducing the general psychical impression, but also a means of registering its mathematical properties. An orthogonal parallel-projection of this virtual image, which in Röntgenology would correspond to the orthodiagram, may be made by tracing taking care to hold the pencil vertically. Similarly a wax or clay image may be modelled by placing the plastic mass in just a position with the stereoscopic image and this either under the Röntgen skiagram or an ordinary stereoscopic image. These *Symphanoplastics* will of course require a certain amount of technical skill, but it should be possible to guide the stylet in this way, so as to shape a model in all respects identical with the original object.

In certain cases it may be of advantage to superimpose a stereo-skiagram and an ordinary photographic stereogram. To do this effectually, the centre of projection of the Röntgen rays must coincide exactly with the centre of projection of the photographic camera. This centre may be taken as the optical centre of the lens-system.

Fig. 8 is a diagram of the *Symphanator*. A is the anticathode, DH the object and P^1 the Röntgen-plate. S is a reflector, making an angle of 45° with the principal axis. The photographic camera with the lens L is placed at the side, at such a distance that Lm is equal to Am. The image on the plate P^2 is smaller than that at P^1, but corresponds exactly with it in perspective. The Röntgen exposure and the photographic exposure may be made simultaneously by making the mirror S of a material which allows the passage of the Röntgen rays. If preferred one exposure may be taken at a time, by using an ordinary mirror, which can be temporarily moved on one side. After the first set of stereoscopic negatives are taken, both the anticathode and the photographic camera are moved to one side over a distance of 65 millimeters. In the figure this displacement is in a direction perpendicular to the paper. We thus obtain two stereoscopic pairs which will give us an ordinary photographic stereogram and a Röntgen stereogram. These may be used in various ways. We may magnify the ordinary photographic negatives to the natural size of P^1, and then place, the Röntgen-plates at P_r and P_l and the photographic pictures at P_r and P_l of figure 7. Of course in that case the large mirrors S^2 and S^2_l must be transparent, whereas the small mirrors may be opaque. In this way we get the two stereo-images superimposed at P so that we may compare one with the other with mathematical accuracy. The Röntgen and the photographic negatives need not necessarily be taken with the same angle of aperture. The skiagram may be taken of only a small area, while the photographic picture may comprise the whole surroundings. We are thus enabled to use small Röntgen plates, a matter of some importance from an economical point of view.

Symphany may also be carried out by using skiagrams that have been reduced in size, the photographic negatives being reduced in the same proportion. By using a "Verant lens-stereoscope" these reductions may be reconstructed of the original size. This is done by placing one pair of pictures behind the lens, and the other pair on the upper part of the stereoscope (see Figure 9). The symphany is effected by means of a transparent mirror placed at an angle of 45°.

It is evident that we may combine symphany with polyphany.

We may now proceed to describe the methods suitable for radioscopic examination with the fluorescent screen.

III. *Metaphany.*

It is often too much trouble for the Röntgenologist to make two stereoscopic pictures. DAVIDSON's method is but seldom employed in practice, probably because it is too laborious and requires a separate apparatus. According to this method the right and the left half-images appear alternately on the screen in rapid succession, the eyes being alternately eclipsed in synchrony, so that each eye sees only the corresponding half-image. This appears to be the only method suitable for stereoscopic vision on the screen, if we adhere strictly to the notion that the stereoscopic sensation consists of two slightly different central projections. We have already shown that this definition is too narrow, since the impression of relief is enhanced if we take more than 2 centres of projection. This is also the case in ordinary vision, where the sensation of relief is produced by the movements of the head. It is not however, the only way in which an impression of relief is brought about psychically, for a one-eyed person is also able to gain the sensation of relief by moving his head to and fro, so that the object may be viewed from more than one side. These different impressions are translated psychically into the relief-image. This resembles to the monocular stereoscopy described by STRAUB. It may also be observed in the kinematograph, where an image, such as a ship, is not shown up in good relief, until it is seen turning round on the screen.

In figure 10 I have depicted the formation of the stereoscopic image on the screen. In DAVIDSON's method the eyes must be exactly

Dr. P. H. EYKMAN. “New methods of stereoscopy.

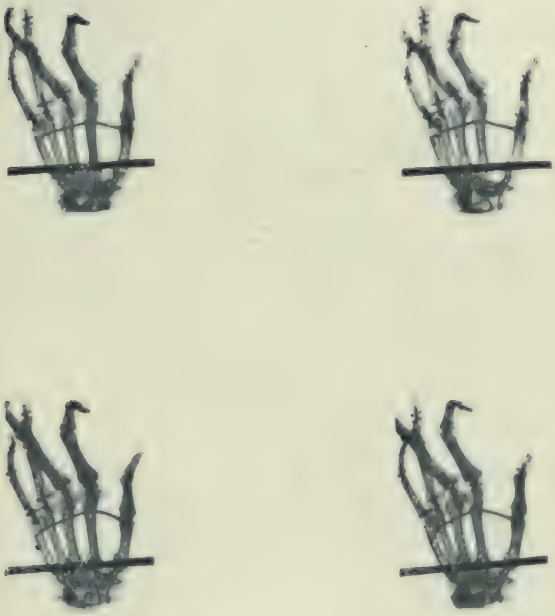

Fig. 1.

Tetraphany. Plate with a set of 4 images.

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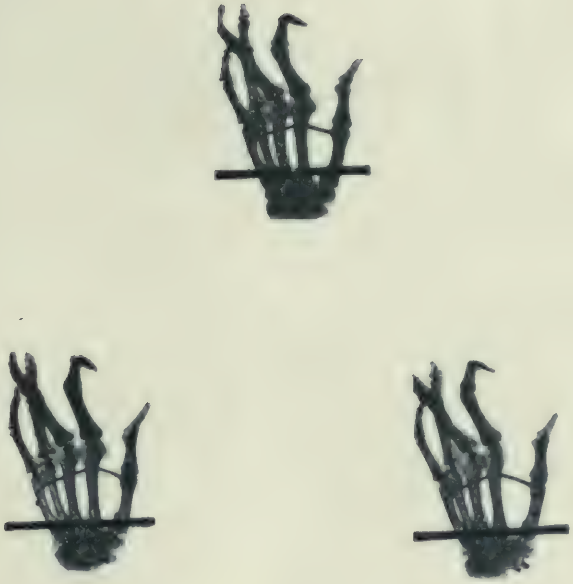

Fig. 3.

Triphany. Plate with a set of 3 images.

opposite the anticathodes and the same distance in front of the screen, as the anticathodes are behind it. In this way we may obtain a complete mathematical reconstruction with this difference, that the stereo-image is a mirror-image of the original object.

A little consideration will show that using one eye only when this eye moves from L' to R' to and fro, while the anticathode R follows the movement from L to R, the eye receives the same impression, as if there were a relief-image on this side of the screen. Psychically one receives a correct impression as to the position of objects, which lie in front and which behind. The distance between R and L, which we supposed to be 65 millimeters may be varied. the displacement may be increased in any direction, transversely, or vertically, backwards or forwards, so long as we are careful to keep the eye exactly opposite the anticathode and the distance of them from the screen identical. When one has realized the fact that we are not looking at the object itself, but at the mirror-image on the screen the appearance of depth and relief is really surprising.

The simultaneous movement of the eye-piece and the anticathode would require a rather complicated apparatus, but the matter may however be simplified, if we restrict the forward and backward motion and permit the anticathode to move only parallel to the screen. The ordinary orthodiagraph may be adapted for this purpose.

In the orthodiagraph the focus tube always moves parallel to the screen. The eye-piece may be connected to the focus tube in such a manner that its aperture is always opposite the anticathode, both focus-tube and eye-piece moving together.

The apparatus may be still further simplified by restricting the downward movement and simply hanging the focus tube by two strings, which only permit a pendulum movement. By this device one may obtain a good impression of the depth and of the relief, when the head follows this pendulum movement of the focus-tube and eye-piece. In figure 11, S is the screen, A_1, A_2 and A_3 are the anticathodes and O_1, O_2 and O_3 the eye-piece in various positions. It is evident that whatever the position of the anticathode the point B which is in contact with the screen, always retains its position. The point D however, which lies nearer, is projected in turn at d_1, d_2 and d_3 and the eye, following the movement, receives the impression that whereas B is situated on the screen, the point D lies at a different depth viz. at D'.

This method serves not only for making a psychical relief-impression, but also for the stereogrammetrical determination of distance. If we suppose the eye to be at O_1 and we direct the line of vision to a point d_1 on the screen, then the point D' which is the image of the foreign body D, will be in the line of vision. We may now bring two points P_1 and P_2 on a wire to coincide with this line of vision. If now the eye is moved to another point, O_3, these two points P_1 and P_2 will no longer be in the line of vision directed to d_3. If now the wire P_1P_2 be moved parallel with itself so that P_1 touches the new line of vision, then the point P will indicate the position of the foreign body. Wherever the eye moves, so long as the anticathode follows the movement, the point P_1 will coincide with the image of D' and is, so to say, closely connected with it. We have now only to measure the distance of P_1 from the screen, in order to know with mathematical accuracy, how far D lies behind the screen. This method I have called *Metaphanometry*.

We may go even further. Let us suppose D to be a foreign body, a bullet for instance. We may place a similar bullet at D'. If now we replace the screen S by a plate-glass mirror, we shall see the reflected image of the bullet D apparently in the patient's body at D, that is in exact coincidence with the bullet in the body, so that the surgeon can proceed to operate as if he had the bullet actually before him. This method we may call *Metasymphany*.

I have come to the above conclusions on theoretical grounds but I have convinced myself by simple models and experiments that the method holds good in practice. I made my first experiments in polyphany and metaphany in FRIEDRICH DESSAUER's laboratory at Aschaffenburg, the first symphanator exposure in Prof. WENCKEBACH's laboratory at Groningen. How far the method may prove of service in practice,can only be determined by long experience and the adaptation of Röntgen instrumentation for the purpose.

(April 22, 1909).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Friday April 23, 1909.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Vrijdag 23 April 1909, Dl. XVII).

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Geophysics. — "*On* Lockyer's 35-*year period in the solar activity.*" By C. Easton. (Communicated by Dr. J. P. van der Stok).

(Communicated in the meeting of March 27, 1909).

In These Proceedings Vol. XI p. 674 the results were communicated of an investigation by Prof. Eug. Dubois on the oscillations in the subsoil water of the dunes of Holland.

From his well known investigations on the flora of the dunes Dr. Vuijck had concluded that almost the whole region of the dunes on our coast is considerably more arid than it was formerly. He supposed that this fact must not be attributed to modifications in the climate, but to several other influences[1]; Prof. Dubois, on the contrary, thinks that we are justified in assuming a periodic rise and fall of the subsoil water. The period of these oscillations would agree in a remarkable way with that which was found by Prof. E. Brückner in many of the meteorological phenomena and which seems to extend over 35 years.

Dr. W. J. S. Lockyer tried to show, in 1901,[2] that a similar period exists in the fluctuations of the solar activity and in terrestrial magnetism. He derived the period mainly from the form and amplitude of the sunspot-curve since 1834: 1. from the modifications in the interval between minimum and maximum in consecutive 11 year periods; 2. from the changing frequency of spots as expressed by the "total spotted area". As the curves for the elements of the terrestrial magnetism are fairly parallel to the sunspot-curve, we have to see in Lockyer's period merely the oscillation in the solar activity. The data, used by Lockyer, are the following: before 1870 those of R. Wolf; then, up to the sunspot-maximum of 1894, those of Ellis and finally the observations of the Solar Physics Observatory near London. From the epochs of the minima and maxima of the solar activity he derives a period of 34.4 years. From the maxima of the magnetic curve this period is found to be 35.25; from the total spotted area 35.5. The total mean is 34.89. For further particulars LOCKYER's article must be consulted.

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[1] L. Vuyck, The flora of the dunes, Leyden, Adriani, 1898, p. 186 and p. 301 sq. In this discussion I think that too little weight is attached (even by Dr. Vuyck himself) to the difference, fully established by V., between the dune-region of our coast (on the mainland) and that of the North-Sea islands. The former is much the more arid. It seems likely that the choking up with sand of the pools in the dunes, which is considered by V. as the main cause of the desiccation of the dunes (not as the only one, as Prof. D. thinks), as well as the climatic changes, must have nearly the same influence on the two regions. — Does not, therefore, this difference rather lead us to consider such technical works as canals, aqueducts etc. as being the main cause of the greater desiccation of the coast region, as compared with the islands?

[2] W. J. S. Lockyer, The Solar Activity 1833–1900. Proc. Roy. Society LXVIII, 1901, p. 285.

The result agrees fairly well with the most probable period derived by BRÜCKNER[1]) from several meteorological phenomena, *viz.* 34.8 ± 0.7 years.

Now it would certainly be extremely important if BRÜCKNER's period were confirmed by the results of an independent investigation. For, though this period — after having been long contested — has become rather popular of late and has been adopted by a great number of meteorologists, particularly in Germany, it still cannot in my opinion be considered as being firmly established. Investigations such as those of Prof. DUBOIS are certainly important for this reason, though of course there may be a difference of opinion about the question whether a 35-year period can really be made out in the series communicated by Prof. DUBOIS.

The 35 year period found by LOCKYER in the solar activity seemed very remarkable therefore. So, for instance, prof. JULIUS HANN writes in his excellent text-book[2]): "Durch die neuerdings aufgestellte 33 bis "35-jährige Sonnenfleckenperiode scheint nun auch eine Ursache für "die 35-jährige BRÜCKNERsche Periode gefunden zu sein." Similarly prof. DUBOIS[3]) writes: "Since W. LOCKYER proved, that in the amount "of spotted area of the sun also a 35-year period could be traced, "from 1833 till 1900, BRÜCKNER's discovery surely has still gained "in importance".

Now, however, we can prove clearly, not only that the 35-year period, which LOCKYER thinks to be traceable in the solar phenomena, is ill founded — this was already pointed out by the author some years ago[4]) — but that the facts which have become known in the last few years have already shown that the English astronomer must be in the wrong.

We will consider successively the two elements: (*A*) $M-m$ (interval in time from a minimum to the next following maximum) and (*B*) *T.S.A.*, from which LOCKYER derived his period. For the reasons mentioned above, the magnetic curve can be left out of consideration. There is, of course, a relation between *A* and *B*. In general the intervals between minimum and maximum become shorter at the time of greater solar activity (highest ordinates of the spot-curve, i.e. greates. Total Spotted Area), and conversely. It is W. Lockyer's merit to have pointed out the importance of the former quantity $M-m$ for several phenomena that may have some connection with the solar activity.

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[1]) ED. BRÜCKNER, Klimaschwankungen seit 1700. Wien. Ed. Hölzel, 1890, p. 272.

[2]) JUL. HANN, Handbuch der Klimatologie Bd I, 3e Aufl. (1908) p. 363.

[3]) DUBOIS l.c. p. 677. See also SUPAN, Grz. Phys. Erdk. IV Aufl. p. 232.

[4]) C. EASTON, Oscillations in the solar activity etc. Proceed. Amst. 26 Nov. 1904. p. 368.

A. — In figure 1 the abscissae represent the years, the ordinates the values of $M-m$. So for instance the ordinate 5.0 for the year 1884.0 represents, according to Lockyer, the interval between the minimum of 1879.0 and the maximum of 1884.0. A similar "minimum to maximum curve" is given by Lockyer for the period 1834—1890, in a figure agreeing with our diagram. L. prolongs his curve, beginning from 1900, by a dotted line, in the expectation that in conformity with the course of the curve between 1867 and 1870 [1]) the fluctuation will rise to a maximum *soon* after 1901. The real course, however, of the solar activity since the time (1900) at which L. established his period, is contrary to his expectation. I now make use of Wolfer's results based on all the principal series of solar observations [2]). It needs no demonstration that the results of these very carefully compared observations — lately 22 series obtained at places all over the earth have been included — furnish the best, or rather the only reliable basis for discussion and cannot be superseded by any single series of observation, such as that of the Solar Physics Observatory. For the rest Wolfer's results agree in the main with those obtained independently in another way and from different materials by Guillaume in Lyons [3]), by Mascari and Riccò at Catania [4]) and by Epstein at Frankfurt on the Main [5]).

Now the mean values of Wolfer for the years since 1867, lead to the following values of the intervals of time $M-m$ in the four last sunspot-cycles:

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[1]) Lockyer's diagrams in Knowledge and Scientific News Vol II. Jan. p. 35, and Fe p. 7, 1905, may be consulted: the predictions quoted above are still more clearly set forth in these passages.

[2]) A. Wolfer, Astron. Mitteilungen XCIII (V. J. S. Naturf. Gesells. Zürich XLVII, 1902) tables II and IV and diagram.

[3]) J. Guillaume, successive volumes of the Comptes-Rendus de l'Ac. d. Sciences, Paris.

[4]) A. Mascari, afterwards A. Ricco, Memorie della Societa degli spettroscopisti Italiani, successive years.

[5]) Th. Epstein, V. J. S. Astron. Gesellschaft 1880—86, and Astr. Nachrichten 4237 (1908). For Epstein's important and too little noticed "Intensivzahlen" see especially. Die Sonnenflecken, Frankfurt a. M., Gebr. Fey. 1904, p. 139.

min. to max.	*months*	*years*
1867—1870	41	3.4
1878—1883	60	5.2
1889—1894	53	4.4
1901—1906	62	5.2

The uncertainty in these values is small for the two first periods, but considerable for the third, because Dec. '88 and Feb. '90 can be equally well taken as the real epoch of the minimum [1]. We have adopted the mean of the two. As to the last maximum: Prof. WOLFER does not as yet venture to fix its epoch definitively, but it appears from already existing data [2] that it *cannot be earlier* than 1906.7. It may easily turn out to be still more retarded by half a year.

The value 5.2 which I assume for *M—m* must be a minimum, therefore [3].

If, in LOCKYER's diagram, we draw the latest part of this curve, it appears to be in contradiction with what was expected by L. Instead of falling steeply it still rises. In my figure I have traced the curve $M—m$ for about a century backwards. Though the reliability of the observations of the sun before the time of SCHWABE's countings must be relatively poor, we are yet justified in expecting that, if the 35 year period really exists, it must still be traceable with some approximation before 1833. The lowest points of the curve ought therefore to coincide approximately with the crosses at the bottom of our diagram, which crosses indicate the epochs of LOCKYER's period. As I have shown already on a former occasion [1], however, there is no trace of such a coincidence.

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[1] A. WOLFER, l. c. vol. XCIII (1902) p. 90 sq:

[2] A. WOLFER, XCIX (1908) p. 288.

Though the author thus anticipates on the results of a still unfinished investigation, he ventures to make the following remarks.

According to WOLFER the present eleven-year period of the sun most clearly resembles that of 1823—34.

The agreement of the highest elevations of the curve is indeed very striking. But we may also compare it to the period 1810—23, which is only still somewhat lower (perhaps as a consequence of incomplete observations) but which in its general form, and with its more advanced centre of gravity, still more closely resembles the present period If we have to do with a real periodicity, and I assume that this is the case, then it will be interesting to ascertain whether the next period (1911—1922 norm.) runs in the same way as the flattened one of 1823—33. About the year 1913 such must be sensible already in the course of the ascending line (the very low values near the minimum too will furnish an indication).

Such indications may prove to be also of importance for terrestrial phenomena. After the maximum we must expect very low winter-temperatures, as in 1830 and 1740.

[3] It is true that EPSTEIN (Astr. Nachr. 4237 p. 205) finds a gradual diminution from the latter half of the year 1905 to the beginning of 1908, but, on account of their inferior completeness, his observations have little weight as compared to WOLFER's series For the rest, what is particularly important is the "table-form" of the smoothed curve 1905—08 as opposed to the summit-form of the curves near 1837 and 1870.

This strong retardation of the observed phase relatively to the computed phase (NEWCOMB, Aph. Journal XIII, 1901, p. 1) was foreseen for the end of a 89-year oscillation of the solar activity. See: Proceed. Amst. 27 May 1905, especially the table of p. 159, in connection with p. 371 and diagram III. These Proc. Nov. 1904.

B. In considering what precedes we feel some surprise at the fact that it has been deemed possible to derive a 35-year period from mutually dependent series of observations, which do not even extend over fully 70 years, i. e. over rather less than two periods. The same remark holds, still more strongly, for the other element: the total spotted area. For even in the diagram of LOCKYER himself the curves for 1847—56 and 1879—90 show but little similarity. Meanwhile it would have been significant (although this would not have demonstrated the existence of the period) if the period 1901—1912 (?) had imitated in form and height those of 1834—1843 and 1867—1879. We have already shown that such cannot be the case as far as the slope of the ascending line is concerned. Further, though the 11-year cycle is not yet complete, the fact has already been established that the curve representing the present period agrees least of all with the two just mentioned ones (as would be required by the 35-year period), nay that it resembles more nearly any other earlier 11-year period.

In order to show this I have reproduced the curves of LOCKYER on the same scale and I have completed them in accordance with WOLFER's curve in the A. M. XCIII [2] — "ausgeglichene Relativzahlen" — further for the years 1901 to 1908, the curve has been drawn from the yearly averages, which have been published afterwards in the A. Mitt. The ordinates thus represent WOLFER's Relativzahlen (100 LOCKYER = 118 WOLFER). For the very latest period I have made use of communications scattered in different papers.

The smoothed yearly "RZ" since 1901 (2.7) are as follows:

1902 : 5.0 1904 : 42.0 1906 : 53.8
1903 : 24.4 1905 : 63.5 1907 : 62.0

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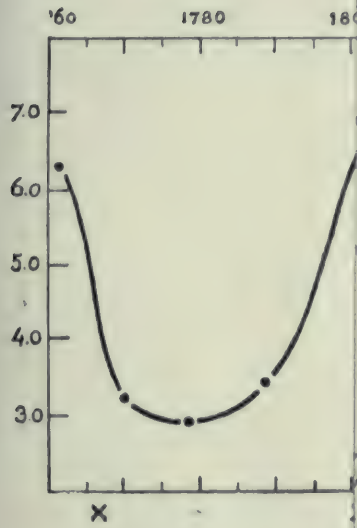
[1] C. EASTON, Zur Periodizität d. solaren und klimatischen Schwankungen, Peterm. Mitteilungen 1905, 8, p. 169.

[2] Also in the Monthly Weather Review, Apr. 1902.



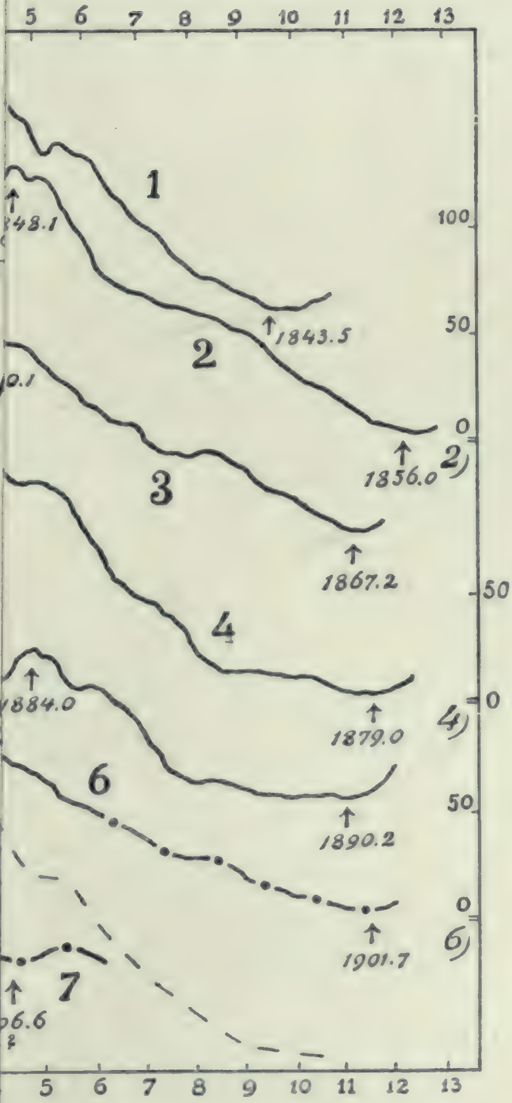


Fig. 2.

pot frequency in the 11-year cycle
since 1834.

In 1908 (3d quarter of the year) another strong increase of the solar activity has taken place, which almost reached the highest monthly averages of 1907 (WOLFER l.c.). On the other hand according to GUILLAUME the 4th quarter of the year showed less than half the spotted area of the preceding three months.

Along with the dotted curve 6—7 (fig. 2) obtained in this way which thus represents the (sufficiently established) true course of the solar activity in this century, I have given a curve (7) consisting of separate dashes. It represents the course which the curve would have shown, if, as required by a 35-year period, N°. 7 had agreed with N^{os}. 1 and 4.[1])

I need not insist that there is not the slightest agreement.

This shows sufficiently that LOCKYER's opinion, according to which a 35-year period should be traceable in the materials now at hand, is untenable.

Mathematics. — "*A family of differential equations of the first order.*"

By Dr. Z. P. BOUMAN. (Communicated by Prof. JAN DE VRIES).

(Communicated in the meeting of March 27, 1909).

Prof. JAN DE VRIES has pointed in These Proceedings Vol. XI (Febr. 27, 1909 p. 756) to a family of differential equations of the first order which are reducible by a projective substitution to a linear equation

$$\frac{dy}{dx} = P(x)\, y + Q(x).$$

Such an equation has the property that the singular point is the vertex of a "critical" pencil of rays, which means that the tangents of the integral curves in the points of each ray meet in *one* point, the "pole" of that ray.

The general form of the equations

$$\frac{dy}{dx} = \frac{f(x, y)}{g(x, y)},$$

belonging to the indicated family can be found in the following manner, in the supposition that f and g are *integer algebraical functions.*

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[1]) "As we are now approaching another maximum of sunspots, which should correspond with that of 1870.8, it will be interesting to observe whether all the solar, meteorological and magnetic phenomena of that period will be repeated" (LOCKYER, Proc. R. S. LXVIII, p. 300).

1. Let $x = 0$, $y = 0$ be a singular point, so that we have $f(0,0) = 0$ and $g(0,0) = 0$.

The tangent to the integral curve in the point (x, mx) is represented by

$$Y - mx = \frac{f_x}{g_x}(X - x),$$

where $f_x = f(x, mx)$, $g_x = g(x, mx)$.

If this tangent is to pass for each value of x through a fixed point, it must be possible to determine x_0 and y_0 in such a way, that for all values of x

$$x_0 f_x - y_0 g_x + (mg_x - f_x)\, x = 0$$

is satisfied.

The left member of this equation must therefore after division by a power of x be linear in x. So we can put

$$f_x = Ax^{n-1} + A'x^n,$$
$$g_x = Bx^{n-1} + B'x^n,$$

and we have then still the condition that $(mg_x - f_x)$ may contain only x^{n-1}.

As f_x and g_x originate from $f(x, y)$ and $g(x, y)$ by the substitution $y = mx$, we can put

$$f = A_0\, y^n + A_1\, y^{n-1}\, x + \ldots + A_n\, x^n + H_1^{(n-1)}(y, x),$$
$$g = B_0\, y^n + B_1\, y^{n-1}\, x + \ldots + B_n\, x^n + H_2^{(n-1)}(y, x),$$

where H_1 and H_2 represent homogeneous polynomia of order $(n-1)$.

Then $mg_x - f_x$ becomes equal to

$$\{(B_0 m^{n+1} + B_1 m^n + \ldots + B_n m) -$$
$$- (A_0 m^n + A_1 m^{n-1} + \ldots + A_n)\}\, x^n + (mB - A)\, x^{n-1}.$$

As $(mg_x - f_x)$ must be, independent of m, of order $(n-1)$ we have the conditions

$$B_0 = 0, \quad B_{k+1} = A_k\ (0 \leqq k < n), \quad A_n = 0.$$

So

$$f = (A_0 y^{n-1} + A_1 y^{n-2}\, x + \ldots + A_{n-1}\, x^{n-1})\, y + H_1^{(n-1)}(y,x),$$
$$g = (A_0 y^{n-1} + A_1 y^{n-2}\, x + \ldots + A_{n-1}\, x^{n-1})\, x + H_2^{(n-1)}(y,x).$$

So we can put

$$\frac{dy}{dx} = \frac{y\, H_3^{(n-1)}(y,x) + H_1^{(n-1)}(y,x)}{x\, H_3^{(n-1)}(y,x) + H_2^{(n-1)}(y,x)} \quad \ldots \ldots \quad (1)$$

Now that the general form of the differential equation has been found, we can easily give the substitution indicated by Prof. DE VRIES.

We can replace (1) by

$$\frac{dy}{dx} = \frac{y}{x} + \frac{H_1^{(n-1)} - \frac{y}{x} H_2^{(n-1)}}{x\, H_3^{(n-1)} + H_2^{(n-1)}}.$$

Let us divide numerator and denominator of the last fraction by x^{n-1}, we then find an equation of the form

$$\frac{dy}{dx}=\frac{y}{x}+\frac{1}{x}\frac{F_1\left(\frac{y}{x}\right)}{F_3\left(\frac{y}{x}\right)+\frac{1}{x}F_2\left(\frac{y}{x}\right)}.$$

Now

$$\frac{dy}{dx}=\frac{y}{x}-\frac{1}{x}\frac{d\left(\frac{y}{x}\right)}{d\left(\frac{1}{x}\right)},$$

so

$$\frac{d\left(\frac{y}{x}\right)}{d\left(\frac{1}{x}\right)}=-\frac{F_1\left(\frac{y}{x}\right)}{F_3\left(\frac{y}{x}\right)+\frac{1}{x}F_2\left(\frac{y}{x}\right)}.$$

By the substitution

$$\frac{y}{x}=u\,,\ \frac{1}{x}=v$$

the equation (1) passes into the linear equation

$$\frac{dv}{du}+\frac{F_3(u)+vF_2(u)}{F_1(u)}=0. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

3. Out of (2) we find at the same time, when the original equation is separated by the substitution:

a. If $F_3(u)\equiv 0$, we have $H_3\equiv 0$, therefore

$$\frac{dy}{dx}=\frac{H_1^{(n-1)}(y,x)}{H_2^{(n-1)}(y,x)},$$

i. e. a homogeneous equation.

b. If $F_2(u)\equiv 0$, so $H_2\equiv 0$, we have

$$x\frac{dy}{dx}=y+\frac{H_1^{(n-1)}(y,x)}{H_3^{(n-1)}(y,x)},$$

and

$$\frac{dv}{du}+\frac{F_3(u)}{F_1(u)}=0\,.$$

c. If $F_1(u)\equiv 0$, we have simply

$$\frac{dy}{dx}=\frac{y}{x}.$$

4. If we approach along the ray $y = mx$ the singular point (0,0) then the tangent of the integral curve is indicated by

$$\frac{dy}{dx} = m + \frac{F_1(m)}{F_2(m) + xF_3(m)}.$$

So in (0,0) we have

$$\frac{dy}{dx} = m + \frac{F_1(m)}{F_2(m)}.$$

5. If the differential equation has the singular point $x = a, y = b$, with critical pencil, then the investigation is reduced to the preceding by a substitution $x = \bar{x} + a,\ y = \bar{y} + b$.

Mathematics. "*On continuous vector distributions on surfaces*". By Dr. L. E. J. Brouwer. (Communicated by Prof. D. J. Korteweg).

(Communicated in the meeting of March 27, 1909).

The theorem, that a differential equation $\frac{dy}{dx} = f(x\,y)$, in which we suppose f to be univalent and continuous, possesses through each point (x_1, y_1) *one* integral curve was proved for the first time by Cauchy[1]) for a field, in which f possesses a continuous partial differential quotient with regard to one of the two variables, and then by Lipschitz[2]) for a field in which the difference quotients of f with regard to one of the two variables for increases of that variable below a certain maximum do not exceed in absolute value a certain maximum.

Peano[3]) finally has done away with all restrictions for f with the exception of its continuity, and has proved, that then still through any point *at least one* (but now in general more than *one*) integral curve exists. It is this result of Peano of which we shall make use to deduce a property of continuous vector distributions on a sphere (or on a surface equivalent to it in the sense of analysis situs, after it has been made measurable by a net of curves which is continuous one-one image of the net of principal circles of a sphere).

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[1]) *Exerc. d'anal.* I, 1840, p. 327; comp. also Moigno, *Leç. sur le calc. diff. et int.*, Tm II (Paris 1844), leç. 26, 27, 28, 33.

[2]) Bull. des sc. math. 10, 1876, p. 149.

[3]) Mathem. Ann. 37, 1890, p. 482; the proof has considerably been simplified by Arzelà, *Sull'esistenza degl'integrali nelle equazioni differenziali ordinarie*, Memorie della Acc. di Bologna (5) 6, 1896, p. 83.

We shall suppose that the vector becomes nowhere zero or infinite; in any point the direction is then univalently determined, and that direction varies continuously from point to point. By placing the sphere into a Euclidean space and by projecting there an arbitrary spherical shell upon its base plane, we then deduce from the theorem of PEANO that in an arbitrary point of the sphere we can at least start *one* single curve, which is *tangent curve* to the vector distribution. Let r be such a tangent curve; we shall then say, that we *pursue* r if we describe it in the direction of the vector and that we "*recur*" it, if we describe it in the direction opposite to the vector.

We now introduce a spherical distance β with the property, that within an arbitrary circle described on the sphere with radius β the *angle*[1]) of any two vectors is $< {}^1/_8\,\pi$.[2]).

Let us now start the curve r in A_0 and let us pursue it up to a point P in such a way, that all points of the described arc A_0P have a distance $< \beta$ from A_0, *then the radius vector drawn from A_0 to an arbitrary point of the arc A_0P will enclose with the direction of the vector in A_0 an angle $< {}^1/_8\,\pi$.* For, if one of the two arcs of principal circles, which in A_0 make an angle ${}^1/_8\,\pi$ with the vector, were transgressed by r between A_0 and P, then according to the supposition the vector is directed in that point of intersection to the inner side of the angle formed by those two circular arcs; so if we pursue r from A_0 to P, it can enter the just-mentioned angle, but it cannot leave it; then however it must always remain inside that angle.

It is likewise evident, that, if T is an arbitrary point on the arc A_0P, the radius vector drawn from T to an arbitrary point of the arc TP encloses with the vector direction in T an angle $< {}^1/_8\,\pi$.

Let Q now be an arbitrary point of r between A_0 and P, we then know that the vector direction has in Q a component in the direction of the radius vector A_0Q; thus, if Q moves along r from

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[1]) For the definition of the angle between two vectors not starting from the same point in an arbitrary non-Euclidean space, comp. these *Proceedings* Vol. IX, 1906, page 121, 122. To determine that angle here on the sphere we transfer the two vectors to a point of the principal circle, which joins them, maintaining their angle with that circle.

[2]) That such a spherical distance β can always be indicated, is evident as follows: If a point D approaches indefinitely to a point C, in which the vector is not zero, then on account of the continuity of the vector distribution also the angle between the vectors in D and C converges to zero, and farthermore that convergence takes place for different points of convergence C *uniformly*, the vector distribution being uniformly *continuous* on account of the sphere being a closed set of points.

A_0 to P, the length of the radius vector A_0Q and likewise that of any radius vector TQ (if T is an arbitrary point already passed) increases continually.

From this we conclude in the first place that between A_0 and P the curve r cannot meet itself and then that, when pursuing r from A_0, *certainly a point B_0 is arrived at, possessing a distance β from A_0*.

For, if such a point were never reached, we could point out on r a series of points

$$G_1 , G_2 , \ldots G_\omega , G_{\omega+1} , \ldots G_\alpha , \ldots$$

which would not end at any number α of the second class of numbers, which points would possess from A_0 the distances

$$\varepsilon_1 , \varepsilon_2 , \ldots \varepsilon_\omega , \varepsilon_{\omega+1} , \ldots \varepsilon_\alpha , \ldots$$

which would continually increase in this order, but remain smaller than β. This however is impossible because the set of the differences

$$\varepsilon_{\alpha+1} - \varepsilon_\alpha$$

must be denumerable.

Any point A_0 is followed by a well-determined point B_0; such an arc A_0B_0 we shall call a β-*arc*; the distance between the end points of a β-arc is β; its length lies between β and $\beta\sqrt{2}$, as is easily seen.

Now in the first place it can occur that the pursuing branch and the recurrent one after a finite number of β-arcs have met either each other or one of the two itself.

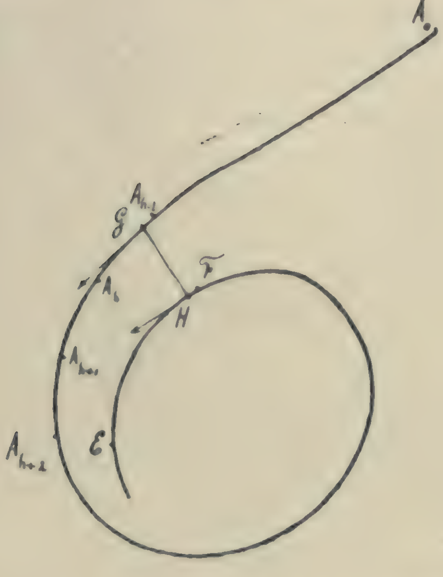
In that case we possess a closed single tangent curve to the vector distribution.

If not, the pursuing branch and the recurrent one can be continued over an infinite number of β-arcs without a meeting taking place; this case we shall investigate more closely.

Let γ be $= {}^1/_2\beta$ and let $A_0 , A_1 , A_2 , \ldots$ be a series of points on r in such a way, that each arc A_nA_{n+1} is a γ-arc. We are now sure that this series of points can reach each finite index. Let fartheron p be an integer greater than the quotient of the spherical surface by the surface of a circle of radius ${}^1/_2\gamma$ on the sphere.

Let us pursue r from A_0 and let us describe round each point A_n a circle with radius ${}^1/_2\gamma$, then two consecutive ones of those circles touch each other on their outside, and any four consecutive circles lie entirely outside each other; however, when A_p is reached, two circles intersecting each other must have appeared, and at the same time or already before, a *first* point F on r must have been reached possessing a distance γ from a point G lying more than a β-arc behind it. If G lies between A_{h-1} and A_h, then A_{h+1} and A_{h+2} have a distance from G which is $> \gamma$, whilst A_h is separated by less than a β-arc from G; so G and F are separated on r by at least three points A.

Let FE be a β-arc, then on FE lies a point H not coinciding with E in such a way, that no other point of that arc has a smaller distance from G. The arc of principal circle GH is then in H perpendicular to r, and as the vector directions in G and H form with each other an angle $< {}^1/_8\,\pi$, they are directed to the same side of that arc of circle. The arc of circle and the arc GH of r have farthermore only their endpoints in common, and they form together a *closed single curve k, of which the length is smaller than* $(p+3)\,\gamma\sqrt{2}$, and which divides the sphere into two domains.



If we pursue r from G, it first runs to H along the boundary of those two domains, and then at H enters one of those domains g_1, *and will leave it no more*, for it no more meets, its own arc GH according to the supposition, and if it were to meet the arc of principal circle GH, that would be at a distance $< \beta$ from H, thus with a pursuing tangent direction, which would *lead* it *into* g_1, but could not make it leave that domain; so this meeting will never be able to take place either [1]).

And analogously, if we recur r from H, it first runs to G along the boundary of the two domains, to enter at G the *other* domain g_2 and leave it no more.

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[1]) On the same grounds it is clear that for r, independent of the choice of A_0, G and H, certainly a minimum distance δ can be pointed out, under which, after the β-arc beginning in H, r will never be able to approach, between the two β arcs beginning in G and in H, the arc of principal circle GH.

Let now γ' be $= \frac{1}{2}\gamma$ and A'_0 (coinciding with H), A'_1, A'_2, ... a series of points on r in such a way, that each arc $A'_nA'_{n+1}$ is a γ'-arc. In the same way as we have constructed the curve k, we now construct a single closed curve k' consisting of an arc $G'H'$ of r, and an arc of principal circle $G'H'$, which is smaller than γ'.

This curve k' lies entirely inside g_1; for after the preceding the only way in which it might still leave it, is that the two arcs of principal circles GH and $G'H'$ should meet in two points, which is impossible, both arcs being $< \pi$.

So the curve k' divides g_1 into 1. an annular domain (which only in the special case that H and G' coincide becomes singly connected), in which lies the arc HG' of r, and 2. a singly connected domain g'_1, within which lies the pursuing branch of r past H'.

Repeating this process indefinitely and taking every time $\gamma^{(n+1)} = \frac{1}{2}\gamma^{(n)}$, we construct a type of order ω of single closed curves, of which each following one lies within the preceding ones, and it is easily proved, that as soon as $\gamma^{(n)}$ has fallen under a certain maximum 1), the following curves $k^{(n)}$ have all a length smaller than $(p+3)\gamma\sqrt{2}$. Hence the lengths of *all* curves $k^{(n)}$ lie below a same finite limit.

We can now regard the place on the sphere of a variable point of $k^{(n)}$ as a function of the length of arc s between $G^{(n)}$ and that point. The different $k^{(n)}$'s are then represented by a system of *uniformly continuous* functions. Thus according to ARZELÀ 2) a fundamental series

$$k^{(\tau_1)},\ k^{(\tau_2)},\ k^{(\tau_3)},\ \ldots$$

can be indicated, *converging uniformly* to a *continuous* limit function $k^{(\omega)}$.

The differential quotients of the functions determining the curves $k^{(\tau)}$ are in any point indicated by the vector direction in that point; they are uniformly approximated by the functions of s determining the difference quotients with respect to s, and they are themselves uniformly continuous functions of s.

So they converge uniformly to a continuous limit function representing the differential quotient, i. e. the tangent direction of $k^{(\omega)}$.

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1) Such a maximum is the quantity δ mentioned in the preceding note. For if we then take $G^{(n)}$ as A_0, and if we construct the corresponding curve k, then the length of the arc between $G^{(n)}$ and the point H belonging to that curve k is smaller than $(p+2)\gamma\sqrt{2}$. We know here however for sure, that, if before this point H no point on r has been reached possessing a distance smaller than δ from $G'^{(n)}$, such a point will not appear farther on either.

2) „*Funzioni di linee*", Rendiconti Lincei (4) 5, 1 (1889), p. 342; "*Sulle funzioni di linee*". Memorie della Accademia di Bologna (5) 5 (1895), p. 225.

So, as any point of $k^{(\omega)}$ is limit point of points of $k^{(n)}$ lying on r, *the limit curve* $k^{(\omega)}$ *is a tangent curve to the vector distribution.*

Farthermore s also represents the length of arc of $k^{(\omega)}$ and as the lengths of the $k^{(\tau)}$'s remain below a same finite limit, $k^{(\omega)}$ also returns into itself after having described a finite length of arc.

The curve $k^{(\omega)}$ cannot reduce to a single point, for then the whole of the directions of the tangents to a curve contracting to a single point would converge to a single direction, namely the vector direction in that limit point, which is impossible.

Neither can a point of $k^{(\omega)}$ belong to two different values of s, unless after a whole circuit; for otherwise $k^{(\omega)}$ would consist of a single closed curve plus points in its "inner domain" (if we call its "outer domain" that in which all curves $k^{(n)}$ lie); which is likewise impossible.

So it is evident that $k^{(\omega)}$ is a single closed curve to which the pursuing branch of r spirally converges uniformly.

In the same way it is evident, that also the recurrent branch of r spirally converges uniformly to a single closed curve $k'^{(\omega)}$ lying entirely outside $k^{(\omega)}$.

The tangent curve r has therefore for analysis situs the character of a double circular spiral circuit, whose two asymptotic closed curves are likewise tangent curves to the vector distribution.

So we possess for continuous vector distributions having in any point a definite direction, at any rate a single closed tangent curve.

Possessing now such a closed tangent curve r_1, we can start another tangent curve in one of the domains determined by the former, which domain we shall call its "inner domain". This curve can behave in different ways:

A. When sufficiently pursued on one side and recurred on the other side, it finally returns into itself without having met r_1.

In this case we possess a single closed tangent curve r_2 bounding a singly connected "inner domain" forming a part of the inner domain of r_1.

B. It does not return into itself inside r_1; here the following cases are possible:

α. When recurring we find it starting somewhere on r_1; when we pursue it, it does not meet r_1. Then according to what precedes it the pursuing branch converges spirally to a single closed tangent curve r_2, bounding a singly connected "inner domain", which is a part of the inner domain of r_1.

β. When recurring we do not find it starting on r_1; when we pursue it however it ends somewhere on r_1. Then the recurrent branch furnishes a single closed tangent curve r_2 with the same property as above.

γ. Neither when we pursue, neither when we recure it meets r_1. It then converges on both sides to a single closed tangent curve. One of these can coincide with r_1; the other however is a single closed tangent curve r_2 with the same property as above.

δ. When we pursue as well as when we recure it meets r_1. The arc lying between the first meeting-points on both sides forms then with an arc of r_1 joining those same points a single closed tangent curve r_2 with the same property as above.

In the same way we can now again enclose a part of the inner domain of r_2 by a single closed tangent curve r_3, and we can construct in this way a fundamental series of single closed tangent curves

$$r_1, r_2, r_3, r_4, r_5, \ldots$$

for which we show, in the same way as above for the curves $k^{(n)}$, that there exists an upper limit for their length of arc and fartheron, that they converge uniformly to a single closed tangent curve r_ω, whose inner domain is a part of that of any curve r_n.

But we can still again let r_ω lose a part of its inner domain by a single closed tangent curve $r_{\omega+1}$, and again $r_{\omega+1}$ by $r_{\omega+2}$, and this process can be continued after any index of the second class of numbers.

On the other hand, however, this is an absurdity, as the system of those losses of domain must remain denumerable.

The supposition, that the vector direction should be determined in any point, has thus proved to be impossible, so that we can formulate:

THEOREM 1. *A vector direction varying continuously on a singly connected, twosided, closed surface must be indeterminate in at least one point.*

And from this follows directly:

THEOREM 2. *A vector distribution anywhere univalent and continuous on a singly connected, twosided, closed surface must be zero or infinite in at least one point.*

If we represent the complex plane stereographically on the NEUMANN sphere, a complex function becomes a vector distribution on the sphere. So we can also interpret our result as follows:

THEOREM 3. *A univalent, continuous function of a complex variable* *being nowhere zero or infinite and without singular points cannot exist*[1]).

Between the above theorem 2 and the property deduced in a former communication [2]) that every continuous one-one transformation with invariant indicatrix of a sphere in itself shows at least *one* invariant point is a close connection. At first sight one might even suppose that they can be directly deduced out of each other. However this is not the case; on the contrary: they complete each other.

Let us namely suppose on one hand the theorem about the vector distribution to be proved. If then is given a continuous one-one transformation of the sphere in itself, we can join each point P with its image P' by an arc of principal circle PP', and consider that arc of circle in size and direction as a vector in P. But the univalence and the continuity of such a vector distribution is now assured only, if for no point P the image lies in the antipodic point; and as this may not be assumed for an arbitrary continuous one-one transformation, a direct appearance of the theorem of the invariant point is excluded.

Let us on the other hand regard as proved the theorem of the invariant point, and let a continuous vector distribution be constructed on the sphere. If we then make the points of the sphere undergo infinitesimal displacements proportionate to the vectors, and if we may suppose these displacements to generate at the limit a one-one transformation (of itself continuous and leaving the indicatrix invariant), we can conclude from it that the vector distribution must of necessity be somewhere zero or infinite. We are, however, sure of the one-one correspondence of that transformation only if by indefinite decrease of the vectors we can make the vector variation anywhere smaller than the corresponding point variation, thus if the infinitesimal difference quotients of the given vector distribution do not exceed a certain maximum. And as in general this condition is not satisfied, the theorem of the vector distribution in its general form does not appear directly as a consequence of the theorem of the invariant point.

A continuous vector distribution on the elliptic plane through a one-two correspondence determining a continuous vector distribution on the sphere, the two following theorems also hold:

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[1]) For *monogenous* complex functions this is a well-known theorem; for, a constant has in the point of the NEUMANN sphere representing the infinite a singular point.

[2]) These Proceedings, page 797 of this volume.

THEOREM 4. *A vector direction varying continuously on a singly connected, onesided, closed surface must be indeterminate at least in one point.*

THEOREM 5. *A continuous vector distribution anywhere univalent on a singly connected, onesided, closed surface must vanish or become infinite at least in one point.*

By the following elementary example theorem 4 is illustrated: If we wish to adjoin in the projective plane by linear relations between the respective coordinates to any point P a straight line passing through that point, this is only possible by taking for that line the line which joins P with a fixed point Q. Theorem 4 informs us that if we wish to select in any point P one of the two half lines joining P and Q, this cannot be done continuously.

We really see that if P moves along a straight line and if at the same time the half line PQ varies continuously, after a circuit of P that half line has not remained the same.

Finally we notice that theorem 5 has as a direct consequence the theorem of the invariant point for the elliptic plane. [1])

For, for a continuous one-one transformation of the elliptic plane in itself the two straight line segments, which join P and its image P', determine, it is true, two oppositely directed vectors, but a selection out of them for *one* point determines a selection everywhere, varying continuously in the whole plane. This is immediately proved, if we let P move along a unilateral curve; P' describes then likewise a unilateral curve, and the selected segment PP', after having varied continuously during the circuit, has remained the same as before.

As farthermore the vector distribution, constructed in this way, becomes nowhere infinite, it must vanish at least in *one* point; this point is invariant for the transformation.

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[1]) These Proceedings, page 798 of this vol.

Physiology. — *"Contributions to the study of serum-anaphylaxis."* (3rd Communication). By Dr. J. G. SLEESWIJK, Foreign Member of the PASTEUR Institute at Brussels. (Communicated by Prof. C. H. H. SPRONCK).

(Communicated in the meeting of March 27 1909).

About Immunity-reactions in serum-anaphylaxis.

It may be assumed on sure grounds that only an intentional application of the methods of the doctrine of immunity will serve to give us some insight into the mechanism of anaphylaxis. Already in my first communication I said something about this subject: among others, that, with the reaction of sensitized animals on the toxic serum-injection alexine is fixed in the organism, and also that already normal blood of the guineapig is able to fix the toxic principle of horse-serum. I then thought I was entitled to put forth the assumption that also other tissues or organs of the guineapig should be capable of such a fixation, a supposition that had also occurred to other investigators, but for which they had found no proofs in their experiments.

However, it is quite possible that the blood corpuscles in this case take up a peculiar position, and that for the supposed fixation of the toxic matter on other organs (e. g. cerebral tissue) the intervention of the bodily fluids of sensitive animals is necessary. Such experiments — as far as I know — have not yet been made. Yet they promise favourable results, especially now that in the meantime I have succeeded in giving a more firm experimental basis to the supposition, likewise put forth in my first communication, that in the sensitized animal the cellular affinity for the here active elements of horse-serum should still be enhanced.

Here we had namely to do with the part of serum and corpuscles of sensitive guineapigs in the anaphylactic reaction. I have herein applied the toxic seruminjection directly in the circulation (carotis), one or a few minutes later I bled the animals to death, and left the blood to itself for some length of time. I surmised namely that, seeing that with this treatment the animals react much quicker and much more violently than with the intraperitoneal injection, probable changes in the biological qualities of the cells or fluids would then also be most striking.

Now if we compare the bloodserum of a sensitive guineapig, treated thus, *before* and *after* the intravascular injection with that of a normal animal treated likewise, we see that in the former a strong haemolysis has manifested itself, which in the latter is hardly perceptible. The hypersensibility, therefore, of the organism is really — and that by the intervention of the anaphylactic guineapig-serum — localized in the red corpuscles, a fact by which a localization also upon other bodily cells is of course by no means excluded, on the contrary rendered probable.

By the side of this haemolysis we now meet with another phenomenon. I have already pointed out before that the disappearance of alexine in vivo can be proved only in intraperitoneally intoxicated animals which do not die, or survive at least half an hour; in other words, to bring about this process some time is necessary. For guineapigs getting the second injection directly into the circulation [1]) and perishing within a few minutes show no loss of alexine. If, however, the blood of an animal treated thus, — defibrinated or not — is for some length of time left to itself in the incubator, the complement may, also under these circumstances, be seen to disappear. In the normal guineapig this process is hardly present, but in the sensitized animal it is much more distinct. This reaction, therefore, if commenced in vivo and set going, also spreads in vitro, only somewhat more slowly.

Now the following question may be asked: does, while these phenomena are coming about, the serum of the hypersensitive animal play an active or a passive part? In order to study this question I was in a position to avail myself of an immunity-phenomenon — the so-called Conglutination-reaction — of which I may as well point out in a few words the origin and the signification.

Ehrlich and Sachs [2]) were at the time the first who drew attention to a peculiar reaction, which takes place between red corpuscles of the guineapig, fresh horse-serum and inactivated cattle-serum. Herein the erythrocytes show a peculiar conglomeration, which can be distinguished from the ordinary agglutinationtype (*con*glutination), followed by a haemolysis. The explanation of this phenomenon has led to a controversy between the schools of Ehrlich and Bordet about the action of amboceptors (sensibilisators) and complement (alexine) — a question with which we do not wish to meddle here. From the publications concerning this subject, by Bordet and Gay [3]),

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[1]) ± 1 cM^3. — The injection-tube with the serum has previously been brought to 37°.

[2]) Berl. Klin. Wochenschr. 1902.

[3]) Ann. Pasteur, 1906.

SACHS and BAUER[1]), BORDET and STRENG[2], the last gave the phenomenon the name of "Conglutinationreaction") it has meanwhile appeared that for the influence of the conglutinating cattle-serum on the guineapig-blood a previous fixation of the horse-alexine to this blood is necessary. Accordingly e.g. the relative complementary power of a horse-serum may in this way be easily determined. But besides it will also be clear that, if in some way or other this fixation of the horse-alexine to the guineapig-erythrocytes can be influenced (either furthered or checked), the course and the result of the whole process may thereby be altered. Now where the just mentioned elements play such an important part in the anaphylactic complex of symptoms, and where we wanted to trace the importance herefor of the serum of sensitized animals, it was also a matter of course to study the influence of such a serum — both before and after the toxic injection — on the course of the conglutinin-reaction. For it was to be expected a priori that the bodily fluids of the guineapigs specifically hypersensitive with respect to horse-serum also in reference to this serum would show some alterations in their qualities.

To bring about the reaction discussed just now, we add together: $^3/_{10}$ cM.^{3} fresh horse-serum with about the double volume ($^6/_{10}$) of the guineapig-serum, then a little physiological solution of sodium-chlorid ($^5/_{10}$), $^1/_{20}$ washed normal guineapig-blood and finally $^2/_{10}$ cattle-serum (during $^1/_2$ hour warmed to 55—56°).

Merely through the presence of normal guineapig-serum the reaction is now somewhat retarded; but important for us is only the comparison of the course of the reaction in the tubes with the anaphylactic guineapig-serum before resp. after the toxic injection. In the main the following facts may be observed:

After the *intraperitoneal* injection of a toxic dose the serum of sensitive guineapigs gets a strong antialexic power with regard to horse-serum, i.e.: it hinders the fixation of the horse-alexine on the guineapig-blood, which is necessary to bring about the conglutination-reaction. Now it is a well-known fact — which I pointed out in my previous communication — that a sensitized guineapig which remains alive after the second intraperitoneal serum-injection (and this depends only on the dose), is rendered immune against a following injection. It may therefore be surmised that the explanation of this fact lies in the just mentioned quality directed against the horse-serum, with which the serum of the animal defends the sensitive elements of the organism (of which the red corpuscles are for us the paradigm) against a toxic injection of the antigen.

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[1] Arb. a. d. Königl. Inst. f. exp. Ther. zu Frankf. a. M. Heft 3, 1907.

[2] Centralbl f. Bakt. Bd. 49, 1909.

After the injection of the horse-serum directly *into the circulation* the serum of the sensitized guineapig shows just the reverse. In the above proportions with the other ingredients brought together to the conglutination-mixture it appears — compared with its action before the toxic injection — to further the fixation of the horse-alexine upon the guineapig-blood. Whence that sharp contrast[1]) in the results of the injections into the abdomen or into the circulation? The contradiction, however, is only a seeming and a relative one. For, it has further appeared to me that, if the last mentioned serum (viz. that of a sensitive animal after the second injection into the circulation) is previously for some hours left in contact with the horse-serum before guineapig-blood and cattle-serum is added — the reaction in this mixture is then strongly retarded in comparison with another mixture, in which all these ingredients are directly added together without any previous mutual contact. It appears therefore that also in this serum after the intravascular injection there are still slumbering unneutralized antihorse-serum qualities, which can be brought to light only in the way just pointed out.

The principal theoretical conclusion which I should like to draw from the above investigations is, that in the (serum-)anaphylaxis we have to do with two contrasting principles: one is the basis of the hypersensibility, the other represents the immunity-principle, and both play a part in the mechanism of the anaphylactic complex of symptoms.

Identification of blood-spots with the aid of anaphylaxis.

Finally I am in a position to communicate here the foundations of a new method to distinguish the blood of man from that of animals and that of different kinds of animals from each other.

I came to this on the ground of what follows. By former investigators it had been proved that with all kinds of sera a specific hypersensibility could be brought about: the same thing in general holds good for the most different proteins, among others also haemoglobin. Because moreover traces of these substances are sufficient, and also granted the fact that the sensitizing principle resists influences from without, it stood to reason for me to try whether these data were to be used for the identification of blood-spots.

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[1]) This does not seem so strange if it is borne in mind that from the abdomen the resorption takes place gradually, whilst with injection into the carotis the circulation is suddenly overflowed by a relatively large quantity of the alien serum. Hence also the different reaction of the organism.

Now I have first dried some drops of blood from different animals (horse, cattle, rabbit) upon small pieces of linen, then extracted them by means of salt-solution and injected the extract subcutaneously into guineapigs in quantities equal to one drop of blood per animal. After the lapse of the usual incubation-stage of 12 or 14 days or longer the animals — as was indeed to be expected — had become hypersensitive to an intraperitoneal injection of 4 or 5 cM.^{3} of the corresponding serum, and that in a quite specific sense. A guineapig e.g., which has been sensitized with the extract from a *cow*bloodspot, and does not in the least react upon an injection of 5 cM.^{3} of *horse*-serum, is as sensitive to an injection of the same quantity of *cow*-serum the day after, as a test-animal — likewise sensitized with extract from a cowbloodspot — but which previously has not been tried with another serum.

Then I have also anaphylactised guineapigs with the extract from spots of human blood. Now as for trying these animals in the subcutaneous or intraperitoneal way rather a great deal of human serum would be necessary, I have examined them upon hypersensibility in the intracerebral way or by preference by intravenous injection. Thus they can very well stand $^1/_5$ cM.^{3} of serum from horse, cattle or rabbit, but the same quantity of human serum, injected into the carotis, kills these animals certainly within a few minutes.

I am busy continuing this investigation, in the hope of rendering the method simpler and more practicable. Meanwhile I have already now intended to point out the principle of this method, because I think it may perhaps find a place by the side of the well-known methods of judicially medicinal investigation of blood.

Physics. — "*Researches on the* JOULE-KELVIN-*effect, especially at low temperatures.* I. *Calculations for hydrogen.*" By J. P. DALTON, M.A., B.Sc., Carnegie Research Fellow. Communication N°. 109^a from the Physical Laboratory, Leiden.

(Communicated in the meeting of March 27, 1909).

§ 1. The present calculations form part of a research which was undertaken [1]) with a view to devising an apparatus for determining the JOULE-KELVIN-effect obtained in expanding helium at the temperature of liquid hydrogen, and thus to lead to some decision regarding the possibility of liquefying helium — an open question at that time. To test the apparatus, expansion experiments were first to be made with air at ordinary temperature, and with hydrogen at the temperature of liquid oxygen; but in the construction of the apparatus it had always to be kept in view that it was eventually to be used in liquid hydrogen. Preliminary experiments showed that the apparatus in its original form did not give a true JOULE-KELVIN-effect, and thus led to a special investigation of the thermodynamics of expansion through a valve and how a valve apparatus has to be arranged so that the enthalpy [1] before and after expansion remains the same. The results of this investigation will be published in this and following communications, for they lose none of their interest by the circumstance that the original object of the research has been disposed of by the liquefaction of helium. [2]

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[1]) The beginning of the research was already referred to in Comm. N^0. 108 (Proc. Aug. 1908).

§ 2. Since the experiments of JOULE and KELVIN [3] of 50 years ago very little experimental work upon similar expansions of gases has been published. This lack of confirmation is rather surprising when we consider the importance of the JOULE-KELVIN experiments in gas-thermometry and the frequency with which their results are employed in various theoretical thermodynamical investigations. With the exception of some rough experiments by REGNAULT [4] upon various gases, and the work of E. NATANSON [5] and KESTER [6] upon CO_2, no further measurements of the JOULE-KELVIN effect seem to have been made. REGNAULT did not obtain results sufficiently definite to lead to any theoretical conclusions, and the results obtained by the other experimenters are not in agreement.

§ 3. Although JOULE and KELVIN began their experiments by allowing the expansion to take place through a small aperture, they soon abandoned that form of apparatus, and used instead a porous plug so as to ensure, by friction in the plug, the immediate conversion into heat of the energy generated, and also to ensure that the expanded gas should issue in a "quiet tranquil stream without jets or rapids". (See § 6, note 1). NATANSON and KESTER also used a porous plug.

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[1] This name has been suggested by KAMERLINGH ONNES to indicate the function $(\varepsilon + pv)$ — the "Heat function" of GIBBS. H. L. CALLENDAR (Phil. Mag. [6]. 5. p. 48. (1903)) calls this expansion "Adiathermal".

[2] H. KAMERLINGH ONNES: Comm. Phys. Lab. Leiden. N°. 108. (Proc. June 1908).

[3] JOULE and KELVIN: Phil. Mag. [4]. 4. p. 481. (1852); Phil. Trans 143. p. 357. (1853); 144. p. 321. (1854); 152. p. 579. (1862).

[4] V. REGNAULT: C. R. 69. p. 780 (1869).

[5] E. NATANSON: Wied. Ann. 31 p. 502 (1887).

[6] F. E. KESTER: Physik. Zeits. 6 p. 44 (1905).
Phys. Rev. 21 p. 260 (1905).

More recently OLSZEWSKI has determined "inversion-points" for various gases, and has returned to the original reduction-valve form of apparatus; but while JOULE and KELVIN's highest initial pressure was not greater than 6 atmospheres, OLSZEWSKI expanded from considerably higher pressures. Since the apparatus to be used in my research resembled that used by OLSZEWSKI, a careful examination of his experimental results and of the criticisms concerning them which have been published was necessary.

§ 4. OLSZEWSKI's first determination [1]) was of an "inversion-point" for hydrogen. This result was subsequently used by PORTER [2]) as a means of discriminating between the validity of certain equations of state. Later OLSZEWSKI investigated [3]) the dependence of inversion temperature upon initial pressure in the case of air and nitrogen, and found that the inversion temperature decreased with falling initial pressure. The results of this research have been criticised in a theoretical investigation recently published by HAMILTON DICKSON. [4]) DICKSON reached the conclusion that OLSZEWSKI's experiment differs fundamentally from that of JOULE and KELVIN. This difference he attributed to the different kinetic energies possessed by the gas in the OLSZEWSKI experiment before and after expansion. It will be shown in a subsequent paper that conduction of heat and loss of pressure in OLSZEWSKI's experiments are probably much more important factors in the result than the change of kinetic energy.

§ 5. DICKSON's criticism was based upon calculations made from VAN DER WAALS's equation of state, but, as this equation is not quantitatively correct, the results obtained are of doubtful value. But if we calculate from the real isothermals of the experimental gas, we ought to obtain close correspondence between the calculated and experimental values of the JOULE-KELVIN effect, in so far as no uncertainty is introduced by errors in the experimental data. To effect such calculations KAMERLINGH ONNES[1]) has given empirical equations of state, which, if specialised for the experimental gas, and, if necessary, between definite limits of temperature and pressure, represent the actual isotherms of the gas to the limits of accuracy of the observations, and in a form easy to manipulate. In this equation the product pv is expressed as a series of five powers of the density; thus

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[1]) K. OLSZEWSKI: Phil. Mag. [6]. 3. p. 535. (1902).
" Ann. Phys. 7. p. 818. (1902).

[2]) A. W. PORTER: Phil. Mag. [6]. 11. p. 554 (1906).

[3]) K. OLSZEWSKI: Phil. Mag. [6]. 13. p. 723 (1907).

[4]) I. D. HAMILTON DICKSON: Phil. Mag. [6]. 15. p. 126. (1908).

$$pv = A + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^4} + \frac{E}{v^6} + \frac{F}{v^8} \quad . \quad . \quad . \quad . \quad (1),$$

where p is expressed in atmospheres, v in terms of the theoretical normal volume as unit, and the "virial-coefficients" $A,B,C,$ etc., are calculated as functions of the temperature from the experimental isotherms of the gas in question, in conjunction with the isotherms of other substances which are brought into relation with the one investigated by means of the law of corresponding states. On this account the equation is usually given in the so-called reduced form:

$$\lambda\mathfrak{p}\mathfrak{v} = \mathfrak{A} + \frac{\mathfrak{B}}{\lambda\mathfrak{v}} + \frac{\mathfrak{C}}{\lambda^2\mathfrak{v}^2} + \frac{\mathfrak{D}}{\lambda^4\mathfrak{v}^4} + \frac{\mathfrak{E}}{\lambda^6\mathfrak{v}^6} + \frac{\mathfrak{F}}{\lambda^8\mathfrak{v}^8} \quad . \quad . \quad . \quad . \quad (2)$$

where λ is equal to $\frac{T_k}{p_k v_k}$, $\mathfrak{p}$ and $\mathfrak{v}$ the reduced pressures and volumes respectively, and

$$\mathfrak{A} = \frac{A}{T_k};\ \mathfrak{B} = \frac{B}{T_k^2}p_k;\ \mathfrak{C} = \frac{C}{T_k^3}p_k^2;\ \text{etc.}$$

§ 6. If the two following experimental conditions are fulfilled, viz.:

1. that the difference between the kinetic energies of the gas before and after expansion is negligible; and

2. that the conduction of heat from the apparatus to the expanding gas is also negligible;

then the expansion process will be represented by the equation

$$\varepsilon_1 + p_1 v_1 = \varepsilon_2 + p_2 v_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(where ε = internal energy of the gas, and the subscripts 1 and 2 refer to the initial and final states respectively) quite independently of whether the expansion has taken place through a valve or a plug[2]), or from a high or low initial pressure. Equation (3) representing an expansion which is characterised by equal values of enthalpy in the initial and final states may by the usual methods[1] be transformed into

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[1]) H. KAMERLINGH ONNES: These Proc. June 1901, and Arch. Néerl. S. II, T. VI, 1901. Comm. Phys. Lab. Leiden. No. 71 and 74.

[2]) In expansion through a valve, since in parts of the jet the kinetic energy temporarily reaches values which are not negligible, intermediate stages of the process are not characterised by equal values of the enthalpy; in expansion through a plug the process, if it agrees with the theoretical suppositions, becomes *isenthalpic*.

$$C_v(T_1-T_2) = \int_{v_1}^{v_2}\left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]dv + p_2v_2 - p_1v_1 \quad . \quad . \quad . \quad (4)$$

or

$$\overline{C_p}\,(T_1-T_2) = -\int_{p_1}^{p_2}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]dp \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where

$$\overline{C}\,(T_1-T_2) = \int_{T_2}^{T_1} C\,dT.$$

Since T_1 and T_2 never differ much in value, and since, in any case, C varies very slowly with temperature, the difference between $\overline{C}$ and C must be extremely small.

For the present calculation equation (4) seems at first sight more directly applicable than (5), but the evaluation of v_2 would necessitate the use of successive approximations; it is, therefore, better to use equation (5). For this purpose, the following transformation, valid as long as excessive densities are not reached, may be applied to equation (2); this equation may be written in terms of reduced pressure as

$$\lambda\,\mathfrak{p}\mathfrak{v} = \mathfrak{A}(p) + \mathfrak{B}(p)\,\mathfrak{p} + \mathfrak{C}(p)\,\mathfrak{p}^2 + \mathfrak{D}(p)\,\mathfrak{p}^3 + \mathfrak{E}(p)\,\mathfrak{p}^4 + etc. \quad . \quad (6)$$

if

$$\mathfrak{A}(p) = \mathfrak{A} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\mathfrak{B}(p) = \frac{\mathfrak{B}}{\mathfrak{A}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$\mathfrak{C}(p) = \frac{\mathfrak{C}\mathfrak{A} - \mathfrak{B}^2}{\mathfrak{A}^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$\mathfrak{D}(p) = \frac{2\mathfrak{B}^3 - 3\,\mathfrak{A}\mathfrak{B}\mathfrak{C}}{\mathfrak{A}^5} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\mathfrak{E}(p) = \frac{\mathfrak{D}\mathfrak{A}^3 - 5\,\mathfrak{B}^4 - 2\,\mathfrak{A}^2\mathfrak{C}^2 + 10\,\mathfrak{A}\mathfrak{B}^2\mathfrak{C}}{\mathfrak{A}^7} \quad . \quad . \quad (11)$$

etc.

Equation (5) in reduced magnitudes becomes

$$\overline{C}_p\,(T_1-T_2) = -\,T_k\,\lambda\int_{\mathfrak{p}_1}^{\mathfrak{p}_2}\left[\mathfrak{t}\left(\frac{\partial\mathfrak{v}}{\partial\mathfrak{t}}\right)_{\mathfrak{p}} - \mathfrak{v}\right]d\mathfrak{p} \quad . \quad . \quad . \quad (12)$$

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[1] See: J. P. Kuenen Die Zustandsgleichung, pp. 106—9 Vieweg 1907.

Since

$$\mathfrak{t}\frac{d\mathfrak{A}}{d\mathfrak{t}} - \mathfrak{A} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

equations (12) and (6) give the relation

$$C_p(T_1 - T_2) = \frac{T_k}{p_k}\left(\mathfrak{t}\frac{d\mathfrak{B}^{(p)}}{d\mathfrak{t}} - \mathfrak{B}^{(p)}\right)(p_1 - p_2) + \frac{T_k}{2p_k^2}\left(\mathfrak{t}\frac{d\mathfrak{C}^{(p)}}{d\mathfrak{t}} - \mathfrak{C}^{(p)}\right)(p_1^2 - p_2^2)$$
$$+ \frac{T_k}{3p_k^3}\left(\mathfrak{t}\frac{d\mathfrak{D}^{(p)}}{d\mathfrak{t}} - \mathfrak{D}^{(p)}\right)(p_1^3 - p_2^3) + \text{etc.} \quad . \quad . \quad . \quad (14)$$

Hence, if we return to the original coefficients by means of (8), (9), (10), (11) and (13), we obtain an expression for the heat-effect in terms of the virial-coefficients, and the initial and final pressures; and if the expansion takes place against atmospheric pressure, this relation becomes

$$(T_1 - T_2) = \frac{\mathfrak{t}\dfrac{d\mathfrak{B}}{d\mathfrak{t}} - 2\mathfrak{B}}{\mathfrak{A}} \cdot \frac{T_k}{C_p p_k}(p_1 - 1) +$$
$$+ \frac{\mathfrak{A}\left(\mathfrak{t}\dfrac{d\mathfrak{C}}{d\mathfrak{t}} - 3\mathfrak{C}\right) - 2\mathfrak{B}\left(\mathfrak{t}\dfrac{d\mathfrak{B}}{d\mathfrak{t}} - 2\mathfrak{B}\right)}{2\mathfrak{A}^3 p_k} \frac{T_k}{C_p p_k}(p_1^2 - 1) +$$
$$+ \frac{3\left(\mathfrak{t}\dfrac{d\mathfrak{B}}{d\mathfrak{t}} - 2\mathfrak{B}\right)(2\mathfrak{B}^2 - \mathfrak{A}\mathfrak{C}) - 3\mathfrak{A}\mathfrak{B}\left(\mathfrak{t}\dfrac{d\mathfrak{C}}{d\mathfrak{t}} - 3\mathfrak{C}\right)}{3\mathfrak{A}^5 p_k^2} \cdot \frac{T_k}{C_p p_k}(p_1^3 - 1) +$$
$$+ \frac{20\left(\mathfrak{t}\dfrac{d\mathfrak{B}}{d\mathfrak{t}} - 2\mathfrak{B}\right)(\mathfrak{A}\mathfrak{B}\mathfrak{C} - \mathfrak{B}^3) + \left(\mathfrak{t}\dfrac{d\mathfrak{C}}{d\mathfrak{t}} - 3\mathfrak{C}\right)(10\mathfrak{A}\mathfrak{B}^2 - 4\mathfrak{A}^2\mathfrak{C}) + \mathfrak{A}^3\left(\mathfrak{t}\dfrac{d\mathfrak{D}}{d\mathfrak{t}} - 5\mathfrak{D}\right)}{4\mathfrak{A}^7 p_k^3}$$
$$\cdot \frac{T_k}{C_p p_k}(p_1^4 - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

which is the equation to be used in calculating the heat-effects.

§ 7. As a first example I have taken hydrogen, and from equation (15) have calculated the heat effects produced when hydrogen is expanded against atmospheric pressure under various conditions of initial temperature and pressure. The values of the virial-coefficients, specialised to fit the isotherms of KAMERLINGH ONNES and BRAAK [1]) down to —217° C. and not yet published, were kindly placed at my disposal by Professor ONNES. These coefficients are

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[1]) H. KAMERLINGH ONNES and C. BRAAK: Comm. Phys. Lab. Leiden. No's 95—101.

$$\left.\begin{aligned}
\mathfrak{A} &= 0{\cdot}0036618\,\mathfrak{t}\\
10^{8}\,\mathfrak{B} &= 168{\cdot}982\,\mathfrak{t} - 435{\cdot}381 - 722{\cdot}848\,\frac{1}{\mathfrak{t}} + \\
&\qquad + 420{\cdot}696\,\frac{1}{\mathfrak{t}^{3}} - 118{\cdot}456\,\frac{1}{\mathfrak{t}^{5}}\\
10^{11}\,\mathfrak{C} &= 50{\cdot}3923\,\mathfrak{t} + 131{\cdot}386 + 131{\cdot}2531\,\frac{1}{\mathfrak{t}} + \\
&\qquad + 199{\cdot}2748\,\frac{1}{\mathfrak{t}^{3}} - 50{\cdot}6347\,\frac{1}{\mathfrak{t}^{5}}\\
10^{18}\,\mathfrak{D} &= 434{\cdot}680\,\mathfrak{t} - 131{\cdot}462 - 903{\cdot}004\,\frac{1}{\mathfrak{t}} + \\
&\qquad + 367{\cdot}7055\,\frac{1}{\mathfrak{t}^{3}} - 178{\cdot}5625\,\frac{1}{\mathfrak{t}^{5}}
\end{aligned}\right\}\quad(16)$$

The values of the critical constants used in the reduction were $p_k = 15$ atm. and $T_k = 29°$ abs.; but as the reduction is ultimately reversed the accuracy or otherwise of these constants is immaterial. The WIEDEMANN value of $C_p = 3.41$ cal. has been used. An estimate of the change of C_p with temperature was obtained by combining equation (2) with the well-known thermodynamical relation

$$C_p - C_v = T\,\frac{\partial p}{\partial T_v}\,\frac{\partial v}{\partial T_p}\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

and regarding C_v as independent of the temperature. 1) This showed that down to —190° C. the variation in C_p at 1 atm. was less than 1%; hence it appeared that a sufficiently high degree of accuracy was reached by retaining the constant value 3.41 throughout these calculations.

For the calculations four terms of equation (2) were found sufficient, for the greatest influence of the $\mathfrak{D}$-term on the values shown in Table I of $T_1 - T_2$ at 100 atm. pressure was not greater than 0°.15. Table I 2) contains the results of the calculations; from it has been constructed the series of $(T_1 - T_2,\ p_1 - 1)_{T=const.}$ curves shown in fig. 1 and also the series of $(T_1 - T_2,\ T_1)_{p_1=const.}$ curves of fig. 2.

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1) Cf. A. W. WITKOWSKI: Bull. de l'Acad. d. Sciences de Crac. Oct.-Nov. 1895. The comparatively great change of C_v and C_p with temperature deduced by H. LE CHATELIER and E. MALLARD. (Séanc. Soc. de Phys. p. 308. (1888)) from experiments at high temperatures cannot be applied to low temperatures without further investigation.

2) The calculation is not extended beyond the limits of density at each temperature at which powers higher than those occurring in (15) must be taken into account.

TABLE I.

t =	10	9	8	7	6.5	6	5	4	3	2
Tabs =	290	261	232	203	188.5	174	145	116	87	58
t° C =	+ 17	− 12	− 41	− 70	− 84.5	− 99	−128	−157	−186	−215
$(p_1 - 1)$ atm.					$T_1 - T_2$					
1	− 0.026	− 0.019	− 0.014	− 0.001	+ 0.006	+ 0.015	+ 0.037	+ 0.073	+ 0.141	+ 0.291
5	− 0.128	− 0.098	− 0.059	− 0.006	+ 0.028	+ 0.071	+ 0.189	+ 0.361	+ 0.698	+ 1.466
10	− 0·259	− 0.198	− 0.121	− 0.016	+ 0.051	+ 0.135	+ 0.351	+ 0.714	+ 1.382	+ 2.951
20	− 0.526	− 0.407	− 0.254	− 0.049	+ 0.081	+ 0.247	+ 0.668	+ 1.371	+ 2.694	+ 5.957
30	− 0.799	− 0.625	− 0.400	− 0.100	+ 0.092	+ 0.335	+ 0.951	+ 1.991	+ 3.931	
40	− 1.080	− 0.852	− 0.558	− 0.166	+ 0.083	+ 0.400	+ 1.200	+ 2.538	+ 5.073	
50	− 1.367	− 1.088	− 0.729	− 0.249	+ 0.056	+ 0.444	+ 1.418	+ 3.044	+ 6.108	
60	− 1.662	− 1.333	− 0.909	− 0.347	+ 0.011	+ 0.467	+ 1.603	+ 3.497	+ 7.023	
70	− 1.963	− 1.587	− 1.102	− 0.460	− 0.052	+ 0.468	+ 1.757	+ 3.897		
80	− 2.270	− 1.849	− 1.306	− 0.587	− 0.132	+ 0.450	+ 1.881	+ 4.246		
90	− 2.584	− 2.119	− 1.520	− 0.729	− 0.229	+ 0.413	+ 1.976	+ 4.544		
100	− 2.904	− 2.398	− 1.744	− 0.885	− 0.343	+ 0.356	+ 2.043	+ 4.793		

§ 8. Considering the a of his equation as a function of the temperature, VAN DER WAALS [1]) deduced the following expression for the JOULE-KELVIN effect:

$$T_1 - T_2 = \frac{2}{mC'_p} \times 273 \left[\frac{a}{v_1} \{2 f(T_1) - T_1 f'(T_1)\} - \frac{RT_1 b}{v_1 - b} \right] . \quad . \quad . \quad (18)$$

and drew attention to the fact that "at a given value of T_1 we may give p_1 such a value that the cooling has a maximum value". The foregoing calculations, the results of which are embodied in Table I, lead to the same conclusion, and show that as the initial pressure increases, the cooling effect (if any) increases, reaches a maximum, diminishes, and finally at high pressures (as long as $\mathfrak{t}_2 > 1$) changes into a heating effect. They show moreover that except in the neighbourhood of temperatures determined by the relation

$$\mathfrak{t} \frac{d\mathfrak{B}}{d\mathfrak{t}} - 2\,\mathfrak{B} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

or at very high pressures, the subsequent terms of the right-hand member of equation (15) are very small compared with the first, and it is therefore only under these circumstances that the progressive change from cooling to heating could be experimentally realised; but if the critical pressure of the gas is low, as in the case of hydrogen, high reduced pressures are easily attainable, and these changes become of importance. In fact, this warming effect obtained in expansions from high pressures explains the fact that TRAVERS [2]) found hydrogen "a perfect gas down to very low temperatures"; for, in his experiments expansions were made from the comparatively high initial pressure of 200 atm. And in this connection it is also worth remarking that in the liquefaction of helium KAMERLINGH ONNES[3]) found that if the expansion pressure exceeded a certain value, the expanding gas no longer showed a cooling effect. The curves (fig. 1 and 2) further show that at lower pressures and at temperatures not in the neighbourhood of those defined by equation (19), the cooling effect remains practically proportional to the pressure-difference, and decreases in magnitude as the temperature of the compressed gas is increased. It was under conditions such as these that the JOULE-KELVIN experiments were carried out, and their results embodied in their well-known empirical equation

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[1]) J. D. VAN DER WAALS. Proc. Kon. Akad. van Wetens. Amsterdam II. p. 379. (1900).

[2]) MORRIS W. TRAVERS: Experimental Study of Gases; p. 197 (1901).

[3]) loc. cit.

$$T_1 - T_2 = \frac{A}{T^2}(p_1 - p_2) \quad . \quad . \quad . \quad . \quad . \quad , \quad . \qquad (20)$$

are in agreement with the foregoing conclusions. The value of A for hydrogen at + 5° C. was given by Joule and Kelvin as — 0.03 which is somewhat greater than the above calculated value of — 0.023; but numerical non-correspondence is in this case of no great importance seeing that Joule and Kelvin's results for hydrogen were very irregular, and the authors declared them to be less trustworthy than those obtained with other gases.

§ 9. With regard to "inversion-points", it is at once evident that the inversion temperature is a function of the initial pressure, and that it does not reach the value $T_{inv} = 7\,T_k$ (see table I). From the curves of fig. 2 have been read the following inversion temperatures corresponding with various initial pressures.

TABLE II.

Pressure-difference	Inversion temperature.
1 atm.	— 72°.6 C.
5 ,,	— 73 .2 ,,
10 ,,	— 74 .1 ,,
20 ,,	— 75 .8 ,,
30 ,,	— 77 .8 ,,
40 ,,	— 79 .9 ,,
50 ,,	— 81 .9 ,,
60 ,,	— 83 .6 ,,
70 ,,	— 85 .9 ,,
80 ,,	— 88 .3 ,,
90 ,,	— 90 .0 ,,
100 ,,	— 91 .7 ,,

Thus the relation between inversion-temperature and pressure-difference is practically linear (fig. 3), and with increasing initial pressure the inversion temperature falls. If we extrapolate the above table we obtain for a pressure of 115 atm. an inversion temperature of — 95° C., where Olszewski found — 80°.5 C. It is worth noting that Nakamura[1]) calculating from Reinganum's equation of state found a value of —79° C. for the inversion point; but in his calculation he seems to have taken no account of the influence of initial pressure and his result is valid only for 1 atmosphere.

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[1]) S. Nakamura: refer. Journ. de Physique (4). 2 p. 704. (1903).

The results obtained by OLSZEWSKI for air and nitrogen are in marked contrast to those here obtained for hydrogen. The diagrams by which he shows graphically the relation between inversion-temperature and pressure, are lines that are strongly curved, and they exhibit, moreover, an inversion temperature increasing with increasing initial pressure. The calculations given above throw some doubt upon these results. For JOULE and KELVIN found for air at ordinary temperatures a linear relation between cooling-effect and pressure difference; this, compared with the foregoing result for hydrogen at — 215° C. renders it highly probable that air and hydrogen follow the law of corresponding states in the JOULE-KELVIN effect, as was to be expected from the facts that their equation of state follows that law, and that both gases are bi-atomic without any chemical complication in the molecule[1]).

Keeping in view this thermodynamic similarity of hydrogen with air or nitrogen it may be inferred from equations (4) or (5) that the inversion temperature curves for all three gases must have the same general properties, and exhibit a relation between inversion temperature and pressure approximately linear; and it can be seen that the small uncertainty in the changes of specific heat with temperature for the different gases cannot account for OLSZEWSKI's finding an opposite effect of initial pressure.

Thus we must conclude that expansion through a reduction-valve of the same construction as that used by OLSZEWSKI does not satisfy the conditions embodied in equations (3) and (15) governing a process at the beginning and end of which the enthalpy has the same value.

A subsequent paper dealing with the experimental portion of this research will show that the cause of this discrepancy can lie in the conditions under which the expansions in OLSZEWSKI's experiments were carried out.

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[1]) Cf. H. KAMERLINGH ONNES: Zitt. Versl. Januari 1896, Comm. Phys. Lab. Leiden. No. 23.

DANIEL BERTHELOT: Journ. de Phys. Mars (1903); and

EDGAR BUCKINGHAM: Bull. Bur. Stand. (3). 2. (1907).

Physics. — "*Researches on the* JOULE-KELVIN *effect, especially at low temperatures.* II. *The* JOULE-KELVIN *effect for air at* 0° *C. and at pressures up to* 42 *atmospheres.*" By J. P. DALTON, M.A., B.Sc., Carnegie Research Fellow. Communication 109^c from the Physical Laboratory, Leiden.

§ 1. In the preceding communication the conclusion was reached that the conditions under which OLSZEWSKI's expansions took place were not those whose fulfilment is necessary for the realisation of a true JOULE-KELVIN process. The present communication offers further justification for that conclusion; it shows that special precautions are necessary before a reduction-valve apparatus, such as OLSZEWSKI used, will give a true JOULE-KELVIN effect, and deals with the experiments leading to, and with the construction of, a reduction-valve apparatus particularly adapted to a determination of JOULE-KELVIN effects at low temperatures. The results obtained with this apparatus in the case of air at 0° C. are in good agreement with those calculated from the isotherms, and also with those experimentally determined by JOULE and KELVIN.

§ 2. The calculation from the isotherms was made in the same manner as that for hydrogen (see § 6 Comm. 109^a). Three terms of the empirical equation of state seemed sufficient for the present purpose. It may, therefore, be written

$$pv = A + \frac{B}{v} + \frac{C}{v^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

and leads to the relation

$$C_p (T_1 - T_2) = \frac{T\dfrac{dB}{dT} - 2B}{A} (p_1 - p_2) +$$

$$+ \frac{1}{2}\left[\frac{A\left(T\dfrac{dC}{dT} - 3\,C\right) - 2\,B\left(T\dfrac{dB}{dT} - 2\,B\right)}{A^2}\right](p_1^2 - p_2^2) \quad . \quad . \quad . \qquad (3)$$

The values of the virial-coefficients for air were kindly placed at my disposal by Professor KAMERLINGH ONNES; at present they are known only for individual isotherms, and, therefore, the evaluation of their rate of change with temperature cannot be made with the same degree of accuracy as was the case with hydrogen; it is, however, sufficiently accurate for the purpose of checking the experimental results. The data employed in the calculation are

$$A_{0^\circ} = 1.0006$$

T	$B \times 10^3$	$C \times 10^6$
0° C.	-0.57440	$+2.9594$
20° C.	-0.40495	$+3.0178$
99°.4C.	$+0.25075$	$+3.5669$

If the value of $C_p = 0.2389$ cal. is used, and if expansion always takes place against atmospheric pressure, equation (3) gives for the cooling effect in air at a temperature of 0° C. the relation

$$T_1 - T_2 = 0.273\,(p_1 - 1) - 0.000208\,(p_1^2 - 1).$$

This is in good agreement with the JOULE-KELVIN experiments which were carried out with pressures up to 6 atm. and satisfied the relation

$$T_1 - T_2 = 0.275\,(p_1 - p_2)\left(\frac{273}{T}\right)^2.$$

§ 3. A diagram of the first apparatus used is shown in fig. 1, and it can be seen that it did not differ much from that described by OLSZEWSKI [1]). Two spirals of copper tubing, s_1 and s_2, joined in series served to bring the gas to the required temperature; s_1, in front of which was coupled a manometer, was 5 m. long and of 3.5 mm. bore; s_2, 7 m. long and of 1.25 mm. bore [2]), ended in a reduction valve K, which opened into a small silvered vacuum-vessel, g. This vacuum glass was enclosed in a german-silver box, B_1, having free communication with the outside through a wide tube, B_2, and was protected from radiation from above by felt faced with nickel-paper. Instead of a resistance thermometer as used by OLSZEWSKI, a thermoelement served to indicate the difference in temperature between the compressed and expanded gas. One junction, Th_1, was in the liquid bath surrounding the spirals, and the second, Th_2, the wires of which were insulated by short glass tubes, b_1 and b_2, soldered into the top of the box, was in the expansion chamber, g. By this means a direct measurement of the heat-effect was possible.

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[1]) K. OLSZEWSKI: Phil. Mag. [6]. 3. p. 535. (1902).
Ann. Phys. 7. p. 818. (1902).

[2]) This cross-section was taken so small on account of the low temperature of the liquid hydrogen in which the apparatus filled with helium was to be placed, and because at that time pure helium was still very difficult to obtain.

§ 4. The thermoelement was Platinum-Constantin, the wires of which had been carefully annealed[1]). The Platinum-Copper junctions were "protected" by copper caps, according to the method generally adopted in this laboratory[2]). The electromotive forces were measured by compensation against a battery of five standard **Weston**-cells in parallel by means of the potentiometer arrangement already published.[3]) The thermoelement was calibrated in steam, oil bath at ordinary temperature, liquid nitrous oxide, liquid air, and liquid hydrogen; in N_2O and liquid air by comparison with a gold resistance thermometer, and in liquid hydrogen by comparison with a platinum resistance thermometer. Both these resistance thermometers had been previously calibrated with the standard hydrogen thermometer.[4]) The sensitivity of this thermoelement is greatly diminished in the neighbourhood of liquid hydrogen temperatures; but at higher temperatures it proved sufficient for the present purpose.

§ 5. Fig. 2 shows the arrangement of the apparatus used for producing the gas-stream and maintaining it at constant pressure. A Brotherhood-compressor, capable of compressing 10,000 litres per hour kept the cylinder C_1, (capacity 25 l.) filled with dry air at a pressure of 70—80 atm., the pressure being indicated by a manometer M. The pressure in the expansion apparatus was regulated by means of the valve K, and its value was indicated by a second manometer attached immediately in front of the first copper spiral.[5]) To intercept any moisture that might have found its way inside the connections, a drying-tube, B, filled with solid KOH was inserted after the valve K. A small pressure cylinder, C_2, of 2—3 litres capacity, surrounded with ice, proved of considerable advantage in keeping the expansion pressure constant and in minimising the disturbing influence of possible irregularities in the flow of gas. After C_2 was coupled the expansion apparatus of fig. 1 with a manometer. The cooling spirals were immersed in water contained in a glass vessel, and this was completely surrounded by ice in a large earthenware pot. Before making a series of experiments, the apparatus was allowed to stand in ice for 3—4 hours, so as to take up the same temperature throughout; the absence of current in the galvanometer showed when the temperature within the expansion chamber was the same as that of the surrounding bath.

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[1]) For experiments with helium at the temperature of liquid hydrogen, the thermocouple gold-silver would be preferable. (See Comm. N^0. 107).

[2]) Comm. Phys. Lab. Leiden N^0. 27.

[3]) Comm. Phys. Lab. Leiden. N^0. 89 (These Proc. Feb. 1904).

[4]) Comm. N . 95^c en 99^c (These Proc. Sept. 1906 and Sept. 1907).

[5]) It will be seen later that the pressure indicated by this manometer was not the actual pressure at which expansion took place.

When an expansion was commenced, the deflection caused by the thermoelectric current in a Hartmann and Braun dead beat galvanometer (Comm. N°. 89, Proc. Nov. 1903) was watched; when the deflection became constant — usually in 3—5 minutes — showing that a steady state was reached, the electromotive force was measured by the potentiometer, accurate compensation being obtained by switching in an astatic Dubois and Rubens protected galvanometer (cf. Comm. N°. 89). When one measurement was completed, the valve K was altered until the next pressure in the series was reached, and the series of operations was repeated.

§ 6. Expansions made with this apparatus were, however, something unusual, as is at once evident from

TABLE I.

Series I. Brass valve A. Air at 0°C. 12/12/07.

(p_1-1)	T_1-T_2
9.7 atm.	warming effect
19.4 „	do.
24.2 „	$+0.86°$ C.
29.0 „	$+1.49$ „
38.7 „	$+2.76$ „
48.4 „	$+4.10$ „

The fact that a warming effect was observed at lower pressures at once led to the suspicion that heat was being conducted along the valve to the expanding gas. During expansion, the gas-jet attains a high kinetic energy, and, correspondingly, an abnormally low temperature, and this kinetic energy is re-converted into heat only when the gas comes to rest after expansion; hence the expanding gas can take up heat from the valve, which, when added to that given by the reconversion of the kinetic energy, causes the final temperature to become too high.

To determine the influence upon the heat-effect of the quantity of gas issuing from the valve, this was opened wider and another series of measurements made.

TABLE II.

Series II. Brass valve *A* Air at 0°C. 12/12/07

(p_1-1)	T_1-T_2
4.8	warming.
9.7	+ 0.34° C.
14.5	+ 1.04 ,,
19.4	+ 1.72 ,,
24.2	+ 2.53 ,,
29.0	+ 3.35 ,,

Hence, increasing the flow of the gas gave increased cooling effects. Further experiments showed that this was so only up to a certain point; at a given pressure difference the cooling effect observed as the valve opening increased soon attained a maximum and diminished as the valve reached its maximum opening; but this was due to the fall of pressure along the spiral, to which further reference will be made in § 9.

The assumption that the irregularity observed is due to heat conduction obtains further support from these experiments, for heat conduction for a given temperature difference between the compressed and expanded gas is constant, while the quantity of cooled gas depends, for a given pressure, upon the opening of the valve.

§ 7. At first it was thought that the conduction of heat was due to the construction of the valve, which was such that the expanded jet had to pass for a short distance along the brass walls of the valve immediately after its formation (see fig. 1). A second valve *B* was then constructed so that the contact of the expanded jet with the material of which the valve was made was reduced to a minimum. Further series of measurements were made with this new valve, but there was no improvement in the results. As before, warming was observed at the lower pressures, and, on opening the valve wider, the cooling observed at any given pressure increased, reached a maximum, and then diminished. The following are the maximum values:

TABLE III.

Series V. Brass valve B. Air at 0°C. 18/2/08.

(p_1-1)	T_1-T_2
3.9 atm.	warming.
7.7 ,,	"inversion"
13.6 ,,	+ 0.67° C.
19.4 ,,	+ 1.58 ,,
27.1 ,,	+ 2.84 ,,
32.9 ,,	+ 3.80 ,,

From this it was evident that heat was being conducted along the metal valve during the formation of the jet, and that as long as a valve made of conducting material was employed the proper adiabatic conditions of expansion could not be fulfilled.

§ 8. It remained to repeat the experiments using a valve of non-conducting material. Preliminary attempts to construct a wooden valve failed, for the wood used was too porous to withstand a pressure of more than a few atmospheres without leakage. Glass was next tried, and gave considerable trouble, for though very carefully annealed, the glass valves frequently broke before a pressure of 20 atmospheres was reached. Glass pins ground so as to close the valves proved quite useless, for the points got constantly broken off and plugged the valve. Eventually a glass valve closed by a wooden pin was used; it was tested up to 70 atmospheres, and although not quite pressure-tight, it closed sufficiently well for the purpose. The metal valve, K, was removed, and the glass one soldered in its place. The glass-copper junction was made according to the method of CAILLETET [1]), by first platinising the glass in the blowpipe, then coppering it electrolytically, and finally, soldering it in the usual way. The junction proved most effective, and successfully resisted a pressure of 70 atm.

§ 9. It is evident from the following results which were obtained with this form of apparatus, that the warming effects previously observed at low pressures have been eliminated by the use of a non-conducting valve.

TABLE IV.

Series XII. Glass valve. Air at 0°C. 30/3/08.

(p_1-1)	T_1-T_2
6 atm.	0.92° C.
11.5 ,,	1.97 ,,
16 ,,	2.78 ,,
21 ,,	3.67 ,,
31 ,,	5.47 ,,
41 ,,	7.37 ,,

That these results, although heat conduction has been successfully eliminated, by no means agree with the JOULE-KELVIN experiments nor with the results calculated from the isotherms in § 2, is due to the fact that the spiral s_2 was so narrow as to cause a considerable fall of pressure along the tube; and at this temperature the pressure fall is too great to allow of the correction being calculated with sufficient accuracy.

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[1]) Comm. Phys. Lab. Leiden. No. 27. (Zitt.versl. Mei en Juni 1896).

This correction became smaller when the narrow tube, s_2, was replaced by two of 2.5 mm. bore in parallel. The following results were thus obtained:

TABLE V.

Series XIV. Glass valve. Air at 0°C. 6/4/08.

(p_1-1)	T_1-T_2
6 atm.	1.054°C.
11 ,,	2.21 ,,
16 ,,	3.35 ,,
21 ,,	4.62 ,,
30 ,,	6.34 ,,

The correction, however, is still too great to allow of its being applied with sufficient accuracy.

In order to ascertain exactly at what pressure expansion was taking place, the apparatus was so altered that a manometer might be attached directly to the expansion valve at the end of the second spiral. This, of course, does not show the true hydrostatic pressure, but calculations of the speed of the gas stream before expansion showed that the difference was negligible.

In the series of expansions undertaken after this change, only one value was obtained, for, on raising the pressure, the valve, which up till now had worked admirably, gave way, and further experiments had to be abandoned. That one value, however, viz.:

Series XV. Glass valve. Air at 0°C. 8/4/08.

(p_1-1)	(T_1-T_2)
5 atm.	1.36°C.

gave a cooling effect of 0.272° C. per atmosphere pressure difference, in good agreement with the JOULE-KELVIN and calculated values.

§ 10. Advantage of the experience gained in these preliminary investigations showing the special difficulties to be guarded against was taken in the construction of a new apparatus. In fig. 3 the apparatus is shown *in situ* in the cryostat into which liquid hydrogen may be introduced. The gas whose JOULE-KELVIN effect is to be determined enters the apparatus by the tube *s*, which is well protected from external sources of heat ; it passes through the spiral s_1; consisting of 10 m. of copper tubing of 3.5 mm. bore, doubly wound, and is there cooled by the vapour arising from the liquid gas in the cryostat : thence it passes to be spiral s_2, which is in the liquid bath at the experimental temperature ; this spiral is also of 3.5 mm. bore, and is 5.3 m. long. The tube *m* leads to a manometer by which the expansion pressure of the gas is indicated. From the spiral s_2, the gas enters the expansion valve, *K*, the flow being regulated by the wooden pin, *p*, and, expanding into the vacuum vessel, *g*, it escapes through the wide tube B_2. As before, the vacuum glass, *g*, is enclosed in a german-silver box, B_1, and is protected from radiation from above A thermoelement, one junction of which, Th_1, is in the liquid bath, and the other, Th_2, in the expansion chamber gives the difference between the temperature of the gas before and after expansion. The method of insulation has been altered, for the glass tubes (b_1 and b_2 in fig. 1) gave continual trouble by breaking at inopportune moments. In the new apparatus the thermoelement wires, enclosed in glass capillaries, are led down through the german-silver tubes b_1 and b_2, from the top of the apparatus. By means of a stirrer, *R*, worked by a string, *t*, passing over a pulley, *k*, the liquid bath is agitated and the temperature kept constant. Heat conduction to the upper portion of the apparatus is minimised by enclosing it in a german-silver cylinder, *c*.

§ 11. A new series of experiments was made with air at 0° C. using this apparatus and the arrangement of fig. 2.

TABLE VI.

Series XVIII. Glass valve. Air at 0°C. 15/3/09.

(p_1-1)	T_1-T_2
2.29 atm.	0.621°C.
4.19 „	1.207 „
9.00 „	2.410 „
14.63 „	4.030 „
18.45 „	5.136 „
23.33 „	6.410 „
28.09 „	7.643 „
28.93 „	7.888 „
32.66 „	8.894 „
37.46 „	10.026 „
42.21 „	11.300 „

The results of this and the previous series of experiments are shown graphically in fig. 4, where the ordinates represent cooling effects and the abscissae observed pressure difference. Values calculated from equation (3) are also plotted, showing good agreement between observed and calculated effects.

§ 12. The question still remained if to the observed results a correction should still have to be applied for possible heat conduction to the gas during expansion. Further experiments were therefore made with a view to determining the influence upon the observed cooling effect of the quantity of gas issuing from the valve. At very small valve-openings, when the quantity of gas expanding was small, the thermoelement registered a temperature that was markedly higher than that obtained with greater valve openings; but as the valve opening increased, the cooling effect rapidly became greater, and a state was soon reached when further increase in the quantity of gas passed through the apparatus had no further measurable influence upon the observed cooling effect.

For instance, with air at 0°C. expanding from a constant pressure of 5.16 atm. the following results were obtained:

Litres per minute.	Cooling. °C p. atm.
5.5	0.244
8.2	0.258
11.4	0.272
12.0	0.273
12.8	0.273
14.0	0.273

That too small a cooling effect was observed at small valve openings may be result of conduction of heat along the glass valve, and of insufficient cooling of the thermoelement (which must constantly receive some heat from outside by radiation and heat-conduction), although, even with the smallest valve openings used, the air in the vacuum glass is swept out in less than a second. The fact, however, that a final condition is reached which is independent of the velocity seems to show that the correction to be applied for heat conduction decreases very rapidly with increasing velocity [1]), and does not come into account in my experiments. The explanation of this circumstance can be given only after further experiments.

§ 13. From the foregoing it is apparent that:

1. For experimental determinations of the JOULE-KELVIN effect

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[1]) At the above pressure, the valve did not allow greater velocities to be used.

with a reduction valve apparatus special precautions must be taken to observe the true expansion pressure, and to ensure absence of heat conduction to the expanding jet.

2. The special apparatus here described gives a JOULE-KELVIN effect for air at 0°C. agreeing with the experimental results of JOULE and KELVIN, and with those calculated from the experimental isotherms.

It is perhaps worth noting that in the practical application of the JOULE-KELVIN effect in the LINDE-HAMPSON process for liquefying gases, in which a reduction valve which is a good conductor of heat is used, heat conduction from the valve to the expanding gas becomes of much less importance than in an accurate determination of the JOULE-KELVIN effect, for in that case the valve and the tube which conducts the gas to it are themselves cooled in the process of regeneration by the expanded gas.

In conclusion, I gratefully acknowledge my indebtedness to Prof. H. KAMERLINGH ONNES, who invited me to undertake this research and to Prof. J. P. KUENEN for their continued interest in my work and for their helpful advice, and also to the CARNEGIE Trust for a grant in aid of the expenses of the research.

Physics. — "*Methods and apparatus used in the cryogenic laboratory. XV. An apparatus for the purification of gaseous hydrogen by means of liquid hydrogen.* By Prof. H. KAMERLINGH ONNES. Communication 109^b from the Physical Laboratory, Leiden.

(Communicated in the meeting of March 27, 1909).

In Communication 94^f (These Proc. Sept. 1906) a liquid hydrogen cycle was described, and attention was drawn to the fact that a continuous action of that cycle was possible only when a sufficient quantity of extremely pure hydrogen was available [1]). In section XI of the communication referred to the method of obtaining this supply was given, The commercial gas was purified by cooling to —205° C.

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[1]) It can easily be seen that obstruction of the regenerator-spiral must necessarily occur when a little air (or oxygen) is present in the hydrogen. The temperature at different heights of the spiral varies with changes in the velocity of the gas stream, which can scarcely be avoided, and, in any case, occur when the circulation is temporarily stopped. The result of this is that the air is alternately frozen, melted, carried lower down in the spiral and again frozen, until finally the opening of the tube is completely plugged.

and [1] by means of a liquid-air (oxygen) separator to such an extent, that, when passed through the hydrogen liquefier it gave a quantity of liquid hydrogen (although comparatively small) before the liquefier became choked, and this liquid, by vaporisation, gave pure hydrogen. When the hydrogen liquefier had again been put in a workable condition, the operations were repeated with a new quantity of gas which had undergone preliminary purification in the liquid-air separator, and the various yields of pure hydrogen thus obtained were carefully collected and united, until the required quantity was available.

This method of operating was rather troublesome, and when once I was in possession of a sufficient quantity of pure hydrogen to keep the cycle in continuous action it was an obvious advantage to avail myself of this cycle for the purification of commercial hydrogen. In Suppl. N°. 19 the communication was already made that an apparatus was being constructed, in which the purification of the hydrogen was effected by means of its liquefaction, while another apparatus had already been constructed in which the impurities were frozen out of the gaseous hydrogen to be purified, by means of the pure liquid hydrogen of the cycle.

The suitability of the latter apparatus has been proved by long use; it is represented in Pl. I and a description of it is here given.

The chief portion of the apparatus is the spiral a_3, in the lower end of which the liquid hydrogen is vaporised; it is placed in a vacuumvessel b, which is closed by means of a cap g. The hydrogen which is to be purified flows through the tube c_3, between the vacuum glass b, and the cylinder d_1, and along the cooled spiral in the opposite direction to that in which the gaseous hydrogen flows away, which is formed by vaporisation inside the spiral. By this means the air contained in the hydrogen is deposited on the windings of the spiral. The purified hydrogen escapes through the paper cylinder d, the copper tubes d_2 and d_3, and the regenerator d_4.

The liquid hydrogen is supplied through a_1, and the insulated tube a_1a_2, to the lower end of the vaporising spiral a_3. To ascertain how much liquid hydrogen must be supplied, the temperature of the purified gas as it enters the cylinder d_1 is determined by means

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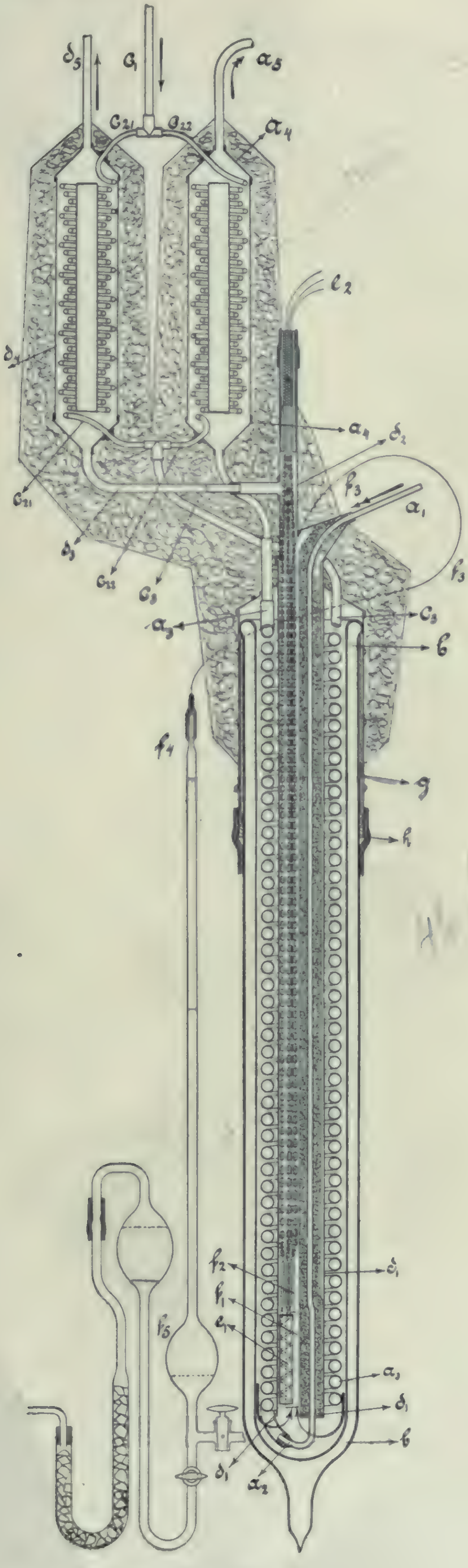
[1] The air separator usually works at a pressure of 60 atm. and with a velocity of 2 $M.^3$ per hour; the impurities remaining do not then amount to more than $^1/_4$ %, and the quantity of liquid air used is about 2 litres per hour. In Comm. 94 the value $^1/_{20}$ % was given: to reach this value, however, the velocity must be much smaller, in order that none of the liquid that separates out should be carried along with the current.

H. KAMERLINGH ONNES. „Methods and apparatus used in the cryogenic laboratory. XV. An apparatus for the purification of gaseous hydrogen by means of liquid hydrogen"



of a hydrogen thermometer. (A resistance thermometer e, is also used: e_1, the cylinder on which the platinum wire is wound, e_2, the leads).

The hydrogen thermometer is arranged exactly the same as the helium-filled control thermometer in the apparatus for liquefying helium. (Cf. Comm. N°. 108 Suppl. to the Proc. June '08) f_1 is the german-silver reservoir, $f_2 f_3$ the steel capillary, f_4 the stem, f_5 the manometer reservoir. The pressure of the hydrogen at 0° C. is chosen so that at the boiling point of hydrogen, the mercury reaches a mark at the upper end of the stem. (The pressure is then 7 cm.). The sinking of the mercury in the thermometer stem gives warning when there is not sufficient liquid hydrogen in the spiral; the supply of liquid hydrogen is so arranged that the mercury oscillates between two fixed marks.

The german-silver cap, g, is attached to the vacuum vessel by means of a rubber sleeve, and projects so far over the vacuum glass that the rubber does not become cold. The upper portion of the cap, g, and the regenerator are protected from external sources of heat by capoc.

As a rule the velocity, with which the hydrogen to be purified is supplied, is so regulated that 5 M³. per hour flow through the apparatus. In that case 4 litres of liquid hydrogen per hour are needed. This rate of production, however, cannot be kept up continuously on account of the fall of pressure in the cylinders containing the hydrogen to be purified, and of various preparatory and auxiliary operations, such as analyses, the coupling and changing of vessels with liquid hydrogen, etc. The time necessary for the manufacture of the liquid hydrogen and for compressing the purified hydrogen into cylinders must also be taken into account. The purification of 10 M³. as a general rule is the work of one day i. e. 8 working hours. On such a working day 25 litres of liquid air are used.

Of course, the purer the hydrogen supplied to it the longer can the apparatus remain in action. Hence, if commercial hydrogen¹) is to be purified, the liquid air separator of Comm. No. 94 sect. XI is coupled to the apparatus here described. If that be done, the apparatus can be worked for hours without stopping. The gas which issues from the apparatus is practically perfectly pure.

It has now become an easy matter to obtain pure hydrogen suitable for liquefaction in the hydrogencycle, if the precaution is taken that a certain minimum store (in Leiden 10 M³.) of pure hydro-

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¹) The percentage impurity changes very irregularly, being sometimes quite small and sometimes very considerable in amount.

gen is always available, which with the present apparatus is now a matter of no difficulty. Formerly, when quite pure hydrogen was a costly commodity, many experiments were obstructed by the precautions necessary to properly collect the hydrogen that had evaporated; but now one need no longer be afraid of sacrificing pure hydrogen, if necessary, and since this is the case, the great objection to its being sent away is removed.

Physics. — "*On the motion of a metal wire through a piece of ice.*" By Dr. J. H. MEERBURG. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of March 27, 1909).

II.

A paper by G. QUINCKE [1]) which had escaped my notice at the time of my first communication on the above-mentioned subject [2]) and which I happened to come across only some time ago, induced me take the subject up again. In this paper by QUINCKE the phenomena are dealt with, caused by occlusions of salt in the ice and it is shown that even with ice, formed from distilled water, these play a part. From this point of view the phenomena are also studied, that are observed when a metal wire sinks through ice; the turbidity where the wire has cut through, is ascribed [3]) to occluded salt-solution with a different refractive power from the ice between which it lies. If this view is right, differences must be expected in the velocity of descent with ice of different origin. For then the slower descent — slower than theory would lead us to expect — is also a consequence of the fact that probably the salt-containing water does not re-freeze above the wire and this cause would be the more effective as the percentage of salt is greater.

So I repeated part of the experiments with ice, formed from distilled water. Boiled distilled water was frozen by means of a mixture of snow and common salt in a glass tube of about 4 cm. diameter, the freezing progressing, after BUNSEN's advice [4]), from above downwards. If the freezing took place sufficiently slowly a quite clear rod of ice was formed in this way [5]). Undoubtedly even this ice contained some salt-solution (dissolved from the glass), according to QUINCKE's observations, but certainly less than the common artificial commercial ice. One experiment was made with ice, formed from water which had been distilled directly through a metal cooler into a vessel of sheet copper, had next been boiled for an hour and then been placed at once outdoors during a frosty night. Of this ice a layer near the wall was clear as glass; nearer the middle it contained small bubbles. Hence the water had not been sufficiently freed from air by boiling or had taken up air again. In the experiment the clear part only was used.

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[1]) G. QUINCKE Ann. d. Phys. **18**. p. 1.

[2]) These proceedings Vol. IX, p. 718.

[3]) G. QUINCKE l. c. p. 46.

[4]) G QUINCKE l. c. p. 14.

[5]) Sometimes a turbidity appeared in the middle of the tube, starting as a plume in the axis, the fine ramifications extending upwards in gentle curves. It is curious

The experiments were made as in my former communication, with a steel wire of 0,4 mm. thickness, cut from the same piece from which I had taken the wire, used in the former measurements. This steel wire had been greased and kept since; it showed no perceptible changes, also under the microscope.

The results of the different measurements are given in the following table[1]).

	P	v	d_1	$2a$	C	Remarks:
1.	2150	3.8	23	76°	0.037	Ice frozen from distilled water in glass tube, perfectly clear.
2.	2150	2.2	36	80°	0.034	Ice frozen from distilled water in glass tube, perfectly clear.
3.	1150	1.2	28	81°	0.027	As before; had lain outdoors during the morning with thaw and so was certainly at 0° at the interior.
4.	2150	2.3	34	83°	0.034	As number one and two.
5.	2150	2.0	32	83°	0.028	Lower part of the piece of number 4, not quite clear, descent irregular.
6.	2150	0.71	91	82°	0.027	Ice from distilled water, frozen in metal vessel.

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that such a plume formed each time the tube had for a moment been removed from the freezing bath, in order to see how far the freezing had proceeded. Thus it could afterwards be seen from the number of plumes how many times this had been done.

[1]) The notations are the same as in the former communication. I avail myself of this opportunity to correct an error in the formulae of that communication. In formulae (1) and (3) the factor 2 in the numerator must be dropped. In the paper by Dr. ORNSTEIN, from which the formulae had been taken, P denoted the weight at either side of the wire; in mine P is the total weight. The values for C are correctly calculated, however: the 2 was dropped in the calculation, so that the mistake had no further consequences.

	P	v	d_1	$2a$	C	Remarks:
7.	2150	2.7	28	79°	0.033	Perfectly clear ice, formed from distilled water with very little Na_2SO_4.
8.	2150	2.3	30	79°	0.030	
9.	2150	2.3	33	80°	0.033	Perfectly clear ice, formed from distilled water with more Na_2SO_4.
10.	1150	1.2	28	80°	0.028	

In the former measurements we found for steel wire of this thickness $C = 0.029$. Here we find as an average (only for ice from distilled water) $C = 0.031$. This difference is scarcely noteworthy, since the theoretical value is about 2.5 times greater. Moreover the values found are slightly too large here, since the fall caused by the piece of ice melting away as a whole, could not be taken into account as in the former experiments, because these pieces contained no bubbles. The ice from the Na_2SO_4- solution gives the same value for C.

In the former communication it was suspected that one of the causes why the calculated value differs from the theoretical one, would be found in a lateral escape of the melting-water. This induced me to observe the wire microscopically during its descent. The microscope used had a magnification of 80; the wire sank at a distance of a few millimetres from a terminal plane of the small ice column and was observed in the microscope with reflected or transmitted light. This at once shows the spots with a refractive power, different from the surrounding parts, mentioned by QUINCKE and explained by him as "solidified foam-bubbles of oily salt-solution". I was able to state distinctly that these spots consist of liquid. Immediately above the wire and at the sides from halfway the height, i.e. where the water is released from pressure, one sees numerous small bubbles which are bright in reflected light and consequently reflect totally. These bubbles are vacua. They often grow and shrink rapidly. As a rule they disappear quickly, but sometimes they grow over a distance of as much as several tenths of a millimetre when the wire sinks, and then are more or less quickly compressed. Also they detach themselves from the wire, rising as globules until they are stopped at a place where by a difference in refractive power an edge is visible. Hence they are stopped by ice that has formed. In a few cases these bubbles are not compressed but remain in existence by being enclosed all round by ice, so that no liquid can flow in. Then they are also distinctly visible macroscopically. The vivid motion of these bubbles over a fairly long distance from the wire proves that liquid is found there and no ice. Although a network of ice is formed in the immediate neighbourhood of the wire, a great part of the water does not freeze. It is exactly for this reason that empty spaces are formed.

Also in the following manner I convinced myself that above the wire much liquid is found. By slightly pulling the wire sideways, putting some cotton-blue on it and then letting the wire go back again, some colouring substance is carried into the block of ice in the immediate vicinity of the wire. If not too much has been introduced, one only sees those spaces coloured where the empty bubbles occurred; the network between them is colourless, since by the formation of ice the colouring substance is excluded. Sometimes a space in which a bubble occurs is seen to shrink near the wire, so that the freezing process can be directly observed. To be sure the introduction of the colouring matter will interfere with the freezing of the melting-water, but very little of the colouring substance is already sufficient for the experiment.

If there are empty spaces above the wire, then — contrary to the former supposition — a flow of water in the piece of ice must be expected from the sides inwardly. In fact I could state this inward flow in a few cases by observing the small solid particles that had entered with the colouring substance. (Experiments with fine chalk particles gave no result). Where a narrow channel existed in the network of ice, the particles were forced through with great velocity and in an inward direction.

The path of the wire consequently consists for a great part of liquid with a network of ice. The liquid is enclosed in this network, for a little cotton-blue, put on the piece of ice where the wire had sunk in, does not penetrate, whereas otherwise this colouring substance enters through the finest channels. If a piece of ice is taken which is not perfectly clear and if then a little of the colouring substance is put on it, the whole piece is in a short time coloured blue all through.

The heat necessary for the melting under the wire is consequently only partly furnished by the solidification above it. The question arises whence the rest of the heat is derived. We may not assume that it is by conduction through the ice. It is not impossible that radiation plays a part here. The following experiment supports this view. If a strong solution of cotton-blue is made to freeze not too slowly in a freezing mixture, the ice which is formed is not clear and has a red-violet tint [1]), the colour of the colouring substance when dry.

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[1]) When the freezing is slow the ice is in this case also perfectly clear and colourless.

Hence the colouring particles are occluded in the ice in a dry condition. Now if this lump of ice is taken from the freezing bath in which it certainly had a temperature of several degrees below zero and is placed in a heated room, it is coloured blue in a few minutes. Hence the colouring particles have caused the ice round them to melt and have dissolved. This change occurs so rapidly that we cannot think of heat conduction. If now a metal wire is present at the interior, this wire will also receive heat through radiation. (At the same time it then becomes clear why a silver wire, as was found in the former experiments, sinks less quickly through the ice than a steel one[1]). I must add that in my experiments an incandescent gas-burner was placed at a short distance from the piece of ice for illumination.

QUINCKE sees in the spots with different refraction above the wire solid masses of foam and oily salt-solution. My experiments show that if it be allowed to speak of salt-solution, it certainly is not solid. But these experiments do not support the view that we have salt-solution here, for then a difference in the rate of descent would certainly have been found between the ice from the salt-solution and the ice from carefully distilled water. The difference in refraction between water and ice is great enough to render the separating surface between them visible. Of course this does not affect the whole of QUINCKE's theory which is founded on an extensive experimental material of which the phenomenon dealt with in this paper is only a subordinate part.

Physics. — "*Contribution to the theory of binary mixtures*", XV. By Prof. J. D. VAN DER WAALS.

SPLITTING UP OF THE SPINODAL LINE.

In the two preceding contributions I have given a description of some shapes of plaitpoint lines for not perfectly miscible liquids. I had suspended the investigation how these shapes depend on possible values of ε_1 and ε_2 in order to describe more fully the shapes of plaitpoint lines obtained by the aid of the theory. And in this description I have for a moment, especially in the case of fig. 41, no longer anxiously questioned whether this plaitpoint line can actually occur on the supposition of positive ε_1 and ε_2. So I shall have to revert to this question later on. But as another very important case of not perfect miscibility can occur, and is at least partially known, I shall, before returning to the interrupted subject, first describe this form, and subject it to a closer investigation.

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[1] These Proceedings 1907, p. 728.

The case that the spinodal line splits up into two parts, is frequently met with for binary mixtures. In this case two *homogeneous* plaitpoints arise, according to KORTEWEG's terminology. And the first example of such a splitting up we met long ago also for perfectly miscible liquids, if minimum T_k occurs. I may consider this case as perfectly known. Then there is also minimum plaitpoint temperature which does not lie much higher than the minimum value of T_k, and occurs for a value of x and v which differs little from that for which this minimum value of T_k occurs. At the moment at which these two plaitpoints originate, we may consider them as a *pair*, but further there is no reason whatever to consider them as conjugate. Then $\frac{dp}{dT}$ for the plaitpoint line is equal to ∞, because $\frac{d^2v}{dx^2}_p = 0$; further $\frac{dT}{dx} = 0$. But $\frac{dp}{dx} = \frac{dp}{dT}\frac{dT}{dx}$ is equal to $0 \times \infty$, and p has neither minimum nor maximum value. I shall leave undiscussed the case that T would have maximum value, in which case the plait would contract to a single point, as this case is unknown for normal substances. As the differential equation of the spinodal line, as I showed in Contribution II, may be written in the form:

$$\left(\frac{dv}{dx}\right)_{spin} = \left(\frac{dv}{dx}\right)_{p=q} \frac{\left(\frac{d^2v}{dx^2}\right)_q}{\left(\frac{d^2v}{dx^2}\right)_p}$$

and in the double point $\left(\frac{dv}{dx}\right)_{spin}$ is undetermined, both $\left(\frac{d^2v}{dx^2}\right)_p$ and $\left(\frac{d^2v}{dx^2}\right)_q$ will have to be equal to 0. The condition for a double point of the spinodal line is therefore, that in such a point both the p-lines and the q-lines present points of inflection. And so, if we wish to know the cases in which splitting up of the spinodal line can take place, we must know the course of the points of inflection of the p- and q-lines, ascertain where the loci represented by $\left(\frac{d^2v}{dx^2}\right)_p = 0$ and $\left(\frac{d^2v}{dx^2}\right)_q = 0$ intersect, and solve the question whether also the spinodal line can pass through such a point of intersection. Both $\left(\frac{d^2v}{dx^2}\right)_p = 0$, and $\left(\frac{d^2v}{dx^2}\right)_q = 0$, has, expressed in x, v, and T, such an intricate form that it seems hardly possible to me to derive the course of these curves from them; but if our purpose is only to form an idea of the points in which these curves intersect, fig. 1 of these Contributions in which the general course of the p-lines is represented, and the following figures, in which the general course of the q-lines is represented, yield sufficient data for this. Most of the properties which I have to discuss, have already been discussed somewhere in these Contributions, and for my purpose it is now only required to collect these scattered observations and perhaps define them a little closer here and there.

With regard to the curve $\left(\frac{d^2v}{dx^2}\right)_p = 0$ it is known that the point in which $\left(\frac{dp}{dx}\right)_v = 0$ intersects the line $\left(\frac{dp}{dv}\right)_x = 0$, viz. the point of intersection with the smallest value of v, is a double point for this curve. From this point starts a branch to the left and one to the right, which remains inside $\left(\frac{dp}{dv}\right)_x = 0$, but which also passes through the double point of $\left(\frac{dp}{dv}\right)_x = 0$ if the temperature is equal to the minimum value of T_k, and also continues to pass on regularly if T is higher and $\left(\frac{dp}{dv}\right)_x = 0$ has broken up into two separate branches: in this case it passes through the critical points of $\left(\frac{dp}{dv}\right)_x = 0$. At not too small a distance from the double point of $\left(\frac{d^2v}{dx^2}\right)_p = 0$ the branch which we discuss here, passes about through the critical points of the mixtures taken as homogeneous. But from this same point of intersection of $\left(\frac{dp}{dx}\right)_v = 0$ and $\left(\frac{dp}{dv}\right)_x = 0$ two more branches proceed to the side of the small volumes. These branches lie on the right and on the left of the curve $\left(\frac{dp}{dx}\right)_v = 0$, and this curve will finally cause them to move to the righthand side.

The righthand branch always passes through the point in which $\left(\frac{dp}{dx}\right)_v$ has minimum volume. A line $p = c$ turns its concave side to the x-axis between the points in which it intersects these two branches of $\left(\frac{d^2v}{dx^2}\right)_p = 0$. But if for sufficiently high value of p these two points coincide, in which case the part of $\left(\frac{d^2v}{dx^2}\right)_p = 0$ which runs from the double point towards smaller values of v, forms a closed curve — this coinciding depends on the shape of the line $v = b$. If the latter is a straight line, as we have assumed in our calculations for the sake of simplicity, coincidence is either excluded or at least very doubtful. But if, what is really more probable, $\frac{d^2b}{dx^2}$ should be positive, the whole p-line over its full width turns its convex side to the x-axis for $p = \infty$, and it no longer intersects the line $\left(\frac{d^2v}{dx^2}\right)_p = 0$. We then conclude that the part of $\left(\frac{d^2v}{dx^2}\right)_p = 0$ which runs from the double point to smaller volumes, is closed, and that the whole curve $\left(\frac{d^2v}{dx^2}\right)_p = 0$ forms one continuous curve, with a double point in the above mentioned point. With rise of the temperature this curve undergoes a change of shape, which it is not necessary for our present purpose to examine in details.

Let us in the same way describe the course of $\left(\frac{d^2v}{dx^2}\right)_q = 0$ in its general features. Also for the course of this curve the presence of $\left(\frac{dp}{dx}\right)_v = 0$ is of the highest importance. If this line is present, and intersects $\left(\frac{d^2\psi}{dx^2}\right)_v = 0$, which then takes place in two points, the lefthand point of intersection is again double point for $\left(\frac{d^2v}{dx^2}\right)_q = 0$. From this double point two branches start, which remain in the region in which $\left(\frac{dp}{dx}\right)_v$ is negative. So the lefthand branch, which runs to the high values of v, continues on the righthand side of $\left(\frac{dp}{dx}\right)_v = 0$, and moves further apart from this line, and the righthand branch passes through that point of $\left(\frac{d^2\psi}{dx^2}\right)_v = 0$, in which this latter curve has maximum volume, and continues to follow the line $\left(\frac{dp}{dx}\right)_v = 0$ in its course at a certain variable distance. The two other branches, which start from the double point of $\left(\frac{d^2v}{dx^2}\right) = 0$, again form a closed curve, which lies on the left of $\left(\frac{dp}{dx}\right)_v = 0$ and which must pass through the point in which $\left(\frac{d^2\psi}{dx^2}\right)_v = 0$ has its minimum volume. In fig. 25, in which $\left(\frac{d^2\psi}{dx^2}\right)_v = 0$ lies on the left of $\left(\frac{dp}{dx}\right)_v = 0$ the case has been drawn, in which $\left(\frac{d^2v}{dx^2}\right)_q = 0$ no longer forms a loop-line. The closed curve, the loop, has then got detached from the other part. This latter part, which, however, has not been represented in fig. 25, then forms a continuous curve in the region in which $\left(\frac{dp}{dx}\right)_v < 0$, always following the line $\left(\frac{dp}{dx}\right)_v = 0$ at a certain variable distance. The loop then passes through the maximum volume and the minimum volume of $\left(\frac{d^2\psi}{dx^2}\right)_v = 0$ [1]), and probably closes on the lefthand side of this curve. In fig. 44 I have drawn the course of the two curves $\left(\frac{d^2v}{dx^2}\right)_p = 0$ and $\left(\frac{d^2v}{dx^2}\right)_q = 0$ for the case that $\left(\frac{dp}{dx}\right)_v = 0$ intersects both $\left(\frac{dp}{dv}\right)_x = 0$ and $\frac{d^2\psi}{dx^2} = 0$, while in fig. 25 the double point of $\left(\frac{d^2v}{dx^2}\right)_q = 0$ has disappeared, and so a closed portion of this curve has detached itself from the other part, and lies entirely on the lefthand side of $\left(\frac{dp}{dx}\right)_v = 0$.

If we now ask where $\left(\frac{d^2v}{dx^2}\right)_p = 0$ and $\left(\frac{d^2v}{dx^2}\right)_q = 0$ intersect, we see that this can only take place more or less in the neighbourhood of $\left(\frac{dp}{dx}\right)_v = 0$, on the left of the point in which this curve has minimum volume. And this being also the place where minimum value of T_k occurs, we may expect the splitting up of the spinodal line for mixtures which have minimum value of T_k.

A first possibility of intersection of the two curves we have below the upper branch of $\left(\frac{dp}{dv}\right)_x = 0$ on the righthand side of $\left(\frac{dp}{dx}\right)_v = 0$. And this occurs in the case which has long been known of minimum plaitpoint temperature for perfectly miscible substances. That also the spinodal line can pass through this point of intersection, and so the p-lines and the q-lines can touch each other, we see when we consider that in that point the q-lines run almost vertically, and that the p-lines in the neighbourhood of $\left(\frac{dp}{dv}\right)_x = 0$ also run almost vertically. But also for not perfectly miscible substances this case occurs, viz. in the case of the preceding contribution represented by fig. 43. By assuming a great value of n in connection with ε_1 and ε_2 below certain limits, we had non-perfect miscibility, while further minimum value of T_k was assumed. I have already pointed out, that the figure given there might undergo some modification according as the component with the smallest value of T_k was also that with the smallest size of the molecules or the reverse. The given figure remains unmodified if the substance with the smallest value of T_k is that which possesses the largest molecule, and might, therefore, serve for mixtures of ether and water. As with increase of the size of the molecules the value of T_k decreases, we must choose from fig. 1 a region lying to the left and as we still assume minimum T_k, we have to put it at a value of x which is only little smaller than 1. Then the discussed point of intersection of $\left(\frac{d^2v}{dx^2}\right)_p = 0$ and $\left(\frac{d^2v}{dx^2}\right)_q = 0$ gets very near to the component with the smallest value of T_k. Let us take ether for this. The splitting up then takes place in such a way, that, as is drawn in fig. 43, the small portion that has got detached contracts into the axis ($x = 1$) with increase of T. So the double point now too almost coincides with the x at which T_k is minimum and lies near the value of v_k for that mixture. Accordingly it would have been better if I had omitted the words (Contribution XIV p. 829) "but for other value of T and x". It is noteworthy that in this case, in which the line $\left(\frac{dp}{dx}\right)_v = 0$ has been quite forced back to the neighbourhood of $x = 1$, the closed detached portion of the line $\left(\frac{d^2v}{dx^2}\right)_q = 0$ lies far apart from $\left(\frac{dp}{dx}\right)_v = 0$; it lies viz. at small value of x, because the curve $\frac{d^2\psi}{dx^2} = 0$ must be found in the lefthand half. So a point of intersection of $\left(\frac{d^2v}{dx^2}\right)_p = 0$ and $\left(\frac{d^2v}{dx^2}\right)_q = 0$, on the left of $\left(\frac{dp}{dx}\right)_v = 0$ and which has been drawn in fig. 44, is not to be expected here. A third point of intersection of these lines, also drawn in fig. 44, on the right of $\left(\frac{dp}{dx}\right)_v = 0$ and for smaller volume than $\left(\frac{dp}{dv}\right)_x = 0$, is of no importance for the splitting up of the spinodal curve — because no points of this line can be present there. There the p- and q-lines can, namely, not touch. The p-lines run there almost parallel to the x-axis, and the q-lines, on the other hand, almost parallel to the v-axis. It follows from all this that if T_k has a minimum value, the splitting up of the spinodal line will take place into what we might call, a righthand branch and a lefthand branch — at least in the case in which the component with the greatest value of b possesses the smallest value of T_k. But this will also be so in the opposite case. Then, however, we must first make the observation that fig. 43 must be modified, or rather that we have then almost entirely the case of fig. 40 back. Then we have to choose a region from the general fig. 1, which begins just before the point, in which T_k has minimum value and further greatly extends to the right. Of course we have also to choose the values n, ε_1 and ε_2 in

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[1]) In fig. 25, however, this particularity has been overlooked, and $\left(\frac{d^2v}{dx^2}\right)_q = 0$ has been drawn erroneously on the right of $\left(\frac{d^2\psi}{dx^2}\right) = 0$.

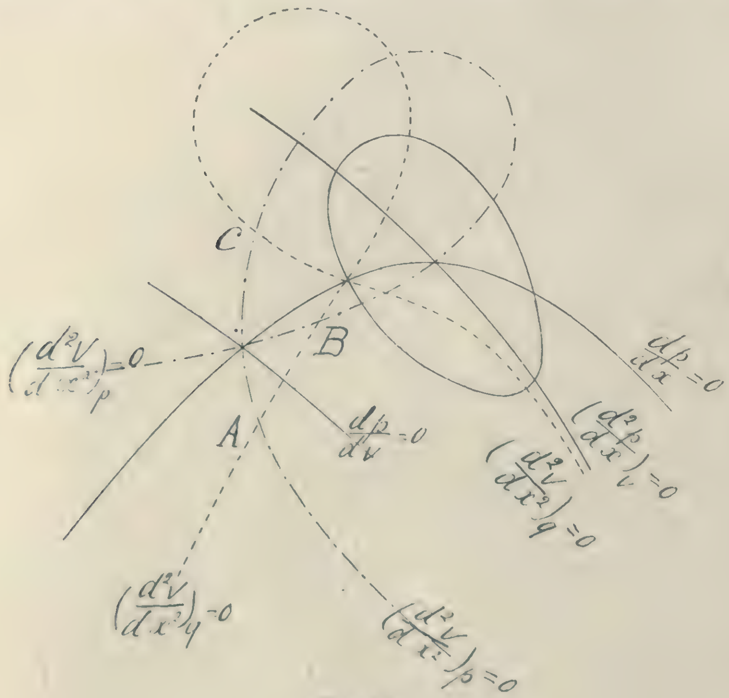
C
$\left(\frac{d^2V}{dx^2}\right)_p = 0$
B
$\frac{dp}{dx} = 0$
A
$\frac{dp}{dv} = 0$
$\left(\frac{d^2p}{dx^2}\right)_v = 0$
$\left(\frac{d^2V}{dx^2}\right)_q = 0$
$\left(\frac{d^2V}{dx^2}\right)_q = 0$
$\left(\frac{d^2V}{dx^2}\right)_p = 0$

Fig. 44.

such a way that not only minimum T_k, but also the intersection of $\frac{d^2\psi}{dx^2}=0$ and $\left(\frac{dp}{dv}\right)_x=0$ takes place, and so incomplete mixture is found. If for such a case we draw a p,x-curve for given T, we are already past the maximum pressure at $x=0$, and the pressure already decreases at $x=0$. On a cursory examination we might think that T_k continually increases. So the p,x-curve has the same shape and the same properties as for the case of fig. 40. But a difference appears in the neigbourhood of the minimum plaitpoint temperature; then the figures 41^a etc. must be modified. Thus e. g. fig. 41^f is the shape of the righthand part at the moment of this temperature, but then there still exists a small closed branch starting from $x=0$, and only at T_{k_1}, which is higher than (T_{pl}) minimum, this branch has entirely retracted into the axis. Then the T,x-projection of the plaitpoint line has, indeed, the descending portion AQ_2, which belongs to the little branch which retracts into the axis $x=0$, but the three-phase-pressure has been modified in so far that the vapour branch, just as in fig. 40, possesses the smallest value of x, and that, therefore, the point of intersection of vapour and liquid branch does not occur at lower temperature. As for $x=0$ we approach nearer to the x of the minimum plaitpoint temperature, the line AQ_2 is smaller and the value of x, at which the splitting up of the spinodal line takes place, is smaller. Not until the initial value of x lies beyond the point with minimum plaitpoint temperature, we get back fig. 41^a etc. The observations made for the mixture CO_2 and urethane suggest the question if for this mixture the initial value perhaps coincides with (T_{pl}) minimum.

In the discussed cases the spinodal line always splits up into a righthand part and a lefthand part, and the splitting up takes place in that point of intersection of $\left(\frac{d^2v}{dx^2}\right)_p=0$ and $\left(\frac{d^2v}{dx^2}\right)_q=0$, which is denoted by A in fig. 44. As mentioned above the intersection of these curves in the point B never gives rise to splitting up of the spinodal curve, because the latter cannot pass through in B. But the intersection in the point C *can* give rise to this, but then into what we may call an upper and a lower part. After the splitting up the lower part surrounds the space inside which $\frac{d^2\psi}{dv^2}$ is negative, and the upper part the space, inside which $\frac{d^2\psi}{dx^2}$ is negative. But as a spinodal line can never intersect the curve $\left(\frac{dp}{dx}\right)_v=0$, unless in a point in which either $\frac{d^2\psi}{dv^2}=0$, or $\frac{d^2\psi}{dx^2}=0$, it is required for the possibility of the splitting up that the curve $\frac{d^2\psi}{dx^2}=0$ lies entirely on the same side of $\left(\frac{dp}{dx}\right)_v=0$ as the point C, which had already been taken into account in fig. 25. It is true if the position of $\frac{d^2\psi}{dx^2}=0$ should be as drawn in fig. 44, a very complicated course for the spinodal line might be imagined, in which this line passes twice through $\left(\frac{dp}{dx}\right)_v=0$, every time touching $\frac{d^2\psi}{dx^2}=0$, but besides with other difficulties, we meet then with the following objection. In this case there must be a point in which $\left(\frac{dv}{dx}\right)_{spin}=\infty$ on the right of $\frac{d^2\psi}{dx^2}=0$ for the spinodal line, which would require $\left(\frac{d^2v}{dx^2}\right)_p=0$. And such a point cannot be pointed out there. At all events we shall assume, if it were only for simplicity's sake, that the position of $\frac{d^2\psi}{dx^2}=0$ is as indicated by the small figure P in fig. 45 [1]). In this figure C represents the double point. At higher temperature the two parts of the spinodal line are quite separated, and they behave independently of each other. On increase of T the spinodal line which belongs to $\left(\frac{dp}{dv}\right)_x=0$ moves to greater volumes, and the spinodal

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[1]) To the solution of the question whether, if the spinodal line belonging to the equilibrium liquid-vapour, is found at a certain value of x, there can occur again a point of a spinodal line for smaller volume, the following equation may contribute

$$\frac{d\left(\frac{d^2\zeta}{dx^2}\right)_{pT}}{dp}=\left(\frac{d^2v}{dx^2}\right)_{pT}.$$

Following the line $x=$ constant, $\int dp\left(\frac{d^2v}{dx^2}\right)_{pT}$ must be $=0$. If dp is always positive, the quantity $\left(\frac{d^2v}{dx^2}\right)_{pT}$ must reverse its sign between two such points. From this follows also that a detached closed longitudinal plait can only occur in a region of fig. 1, where the circumstance occurs that for small volumes $\left(\frac{d^2v}{dx^2}\right)_{pT}$ is negative.

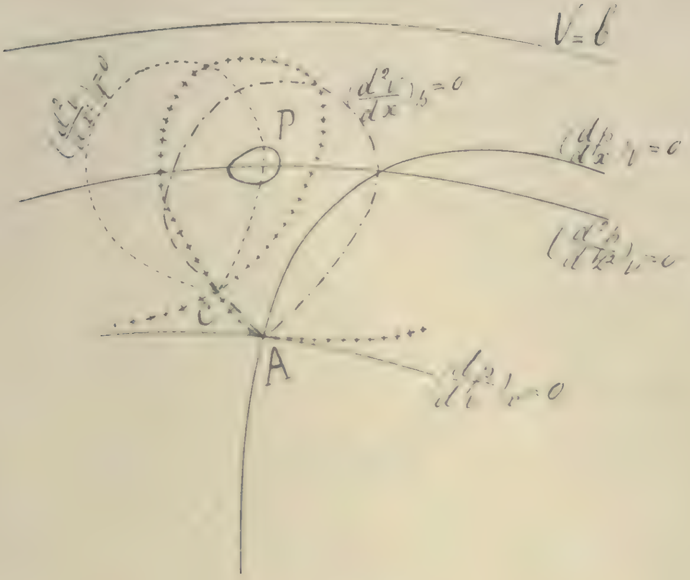
$V=b$
$\left(\frac{d^2\psi}{dx^2}\right)_v=0$
P
$\left(\frac{dp}{dx}\right)_v=0$
$\left(\frac{d^2p}{dx^2}\right)_v=0$
C
A
$\left(\frac{dp}{dv}\right)_x=0$

Fig. 45.

line which runs in the neighbourhood of $\frac{d^2\psi}{dx^2}=0$, contracts.

If the point C is to exist, in the first place the point A, the point of intersection of $\left(\frac{dp}{dx}\right)_v=0$ and $\left(\frac{dp}{dv}\right)_x=0$ must occur; and from this follows that the value of x, in which T_k is minimum, is not too small. In the case that we supposed above, the value of x for T_k minimum was so small, that the point A did not exist for it, or would have to be supposed to occur for negative values of x. In other words: this splitting up of the spinodal line is only possible if the value of x, for which T_k is minimum, is not very small. Moreover, the condition is, of course, that $\frac{d^2\psi}{dx^2}=0$ shall disappear outside the region in which $\frac{d^2\psi}{dv^2}$ is positive. But this splitting up of the spinodal line again requiring that T_k has minimum value, we may put as a general rule that only if T_k shows minimum value, splitting up of the spinodal line can occur.

But not only the point A must be present, if the discussed splitting up of the spinodal line is to take place, but of course also the point C itself: and the existence of the entire detached closed portion of the spinodal curve even demands that the point C shall occur for not too small a value of x — though the limiting value is not to be indicated, and though it will diverge greatly for the different cases.

At the temperature of the splitting up the point C lies on the binodal line of the equilibrium liquid-vapour. This point is then at the same time the plaitpoint of the detached plait, which we may call longitudinal plait, and which also possesses a binodal curve for the equilibrium of two liquids. If $\frac{d^2b}{dx^2} > 0$, in accordance with which I have drawn the line $v = b$ curvilinear, this longitudinal plait is closed. Then the spinodal line of this longitudinal plait, which has also been drawn in fig. 45, has a point with minimum volume, where it passes through $\left(\frac{d^2v}{dx^2}\right)_q = 0$. There are also points where $\left(\frac{dv}{dx}\right)_{Spin} = \infty$, i.e. where it cuts $\left(\frac{d^2v}{dx^2}\right)_p = 0$. The sign of $\left(\frac{dv}{dx}\right)_{Spin}$ is determined by the given differential equation, and quite corresponds with the values of $\frac{dv}{dx_p}$, $\left(\frac{d^2v}{dx^2}\right)_p = 0$ and $\left(\frac{d^2v}{dx^2}\right)_q = 0$ in fig. 45. The value of $\left(\frac{dv}{dx}\right)_p$ is always positive, because this spinodal curve lies in the region where $\left(\frac{dp}{dx}\right)_v > 0$. And the signs of the two other quantities are negative inside and positive outside the limits for which they are 0. For this longitudinal plait there is indeed equilibrium between two liquids, but not with a third phase. So it lies altogether outside the region of three-phase-pressure.

If we trace the p,x-line for the equilibrium liquid-vapour, both $\frac{dp}{dx}$ and $\frac{d^2p}{dx^2}$ is equal to 0 for the point C. At somewhat lower temperature, viz., longitudinal plait and transverse plait overlap slightly, as they both extend with decrease of temperature. Then there is, indeed, three-phase-pressure; then there is coexistence of 2 liquids and vapour. The metastable and unstable branch, which exists for this equilibrium between the two coexisting liquids, has a minimum and a maximum. In the point C not only the two points of equal pressure coincide but also the minimum and the maximum pressure. In the v,x-projection of the binodal curve for the equilibrium liquid-vapour we have in the point C:

$$\left(\frac{dv}{dx}\right)_{bin} = \left(\frac{dv}{dx}\right)_p$$

and

$$\left(\frac{d^2v}{dx^2}\right)_{bin} = \left(\frac{d^2v}{dx^2}\right)_p = 0.$$

Though these equations hardly require a proof, I may point out that they can also be directly derived from:

$$\left(\frac{dp}{dx}\right)_{bin}=\left(\frac{dp}{dv}\right)_x\left(\frac{dv}{dx}\right)_{bin}+\left(\frac{dp}{dx}\right)_v$$

and

$$\left(\frac{d^2p}{dx^2}\right)_{bin}=\left(\frac{dp}{dv}\right)_x\left(\frac{d^2v}{dx^2}\right)_{bin}+\left[\frac{d^2p}{dv^2}\left(\frac{dv}{dx}\right)^2_{bin}+2\frac{d^2p}{dx\,dv}\left(\frac{dv}{dx}\right)_{bin}+\frac{d^2p}{dx^2}\right].$$

As

$$0=\left(\frac{dp}{dv}\right)_x\left(\frac{dv}{dx}\right)_p+\left(\frac{dp}{dx}\right)_v$$

and

$$0=\left(\frac{dp}{dv}\right)_x\left(\frac{d^2v}{dx^2}\right)_p+\left[\frac{d^2p}{dv^2}\left(\frac{dv}{dx}\right)^2_p+2\frac{d^2p}{dx\,dv}\left(\frac{dv}{dx}\right)_p+\frac{d^2p}{dx^2}\right]$$

If $\left(\frac{dp}{dx}\right)_{bin}=0$, $\left(\frac{dp}{dv}\right)_x\left[\left(\frac{dv}{dx}\right)_{bin}-\left(\frac{dv}{dx}\right)_p\right]$ must be $=0$, or $\left(\frac{dv}{dx}\right)_{bin}=\left(\frac{dv}{dx}\right)_p$ and $\left(\frac{d^2p}{dx^2}\right)_{bin}=\left(\frac{dp}{dv}\right)_x\left[\left(\frac{d^2v}{dx^2}\right)_{bin}-\left(\frac{d^2v}{dx^2}\right)_p\right]$.

If $\left(\frac{d^2p}{dx^2}\right)_{bin}=0$, then $\left(\frac{d^2v}{dx^2}\right)_{bin}=\left(\frac{d^2v}{dx^2}\right)_p$, and as the latter quantity is zero in the point *C*, also $\left(\frac{d^2v}{dx^2}\right)_{bin}=0$.

In the point for the equilibrium liquid-vapour, in which the two phases have equal concentration, $\left(\frac{dp}{dx}\right)_{bin}$ is indeed $=0$, but $\left(\frac{d^2p}{dx^2}\right)_{bin}$ is negative. For this point $\left(\frac{dv}{dx}\right)_{bin}=\left(\frac{dv}{dx}\right)_p$; but taking into account that $\left(\frac{dp}{dv}\right)$ is negative, we find for this point $\left(\frac{d^2v}{dx^2}\right)_{bin}>\left(\frac{d^2v}{dx^2}\right)_p$.

But at the same time we may now also draw attention to the following important property. The point in which for liquid and vapour the concentration is the same, so where $\left(\frac{dp}{dx}\right)_{bin}=0$, or p maximum, lies at smaller value of x than that of the point *C*. This property holds certainly if we may assume it to be of general validity that if a p-line touches a binodal curve of a plait, the curvature of this p-line is always such that the plait lies on its concave side. For a plaitpoint this is certainly the case. But the question is whether we may also accept it as valid for that point of a binodal line in which the value of p is maximum. Then $\left(\frac{d^2v}{dx^2}\right)_p$ and a fortiori

$\left(\frac{d^2v}{dx^2}\right)_{bin}$ is positive on the side of the small volumes. On the side of the great volumes $\left(\frac{d^2v}{dx^2}\right)_{bin}$ is also positive, and so turned from the plait, but $\left(\frac{d^2v}{dx^2}\right)_p$ is negative there. For the proof it would be necessary to examine how a cone differing little from a plane, resting with its apex in an horizontal plane, and the generatrices of which ascend towards the side of the small volumes, envelops two convex-convex parts of a surface. The points of contact give the value of $\left(\frac{d^2v}{dx^2}\right)_{bin}$. If we examine besides how a cylindre the generatrices of which run parallel to the generatrix of the cone, as it is in the plane parallel to the v-axis, envelops the two parts of the convex-convex surface, we find the value of $\left(\frac{d^2v}{dx^2}\right)_p$. I draw attention to the fact that for the mixture water and phenol SCHREINEMAKERS has experimentally shown that at the temperature at which the point C exists, the relative situation of the two points is, as is given here as a rule of general application. On the liquid side $\left(\frac{dp}{dv}\right)_x$ is so large negative that unless $\left(\frac{d^2p}{dx^2}\right)_{bin}$ is also very great negative, the difference between $\left(\frac{d^2v}{dx^2}\right)_{bin}$ and $\left(\frac{d^2v}{dx^2}\right)_p$ is scarcely appreciable. And the first of these quantities being positive, this is also to be expected for the second.

But yet thermodynamically or purely mathematically this property is not to be generally proved. It follows, however, if the equation of state is applied. If we namely draw the locus of the points of intersection of the two curves $\left(\frac{dp}{dv}\right)_x = 0$ and $\left(\frac{dp}{dx}\right)_v = 0$, we find $\frac{v}{b} = 2\frac{\frac{1}{b}\frac{db}{dx}}{\frac{1}{a}\frac{da}{dx}}$, and for the locus of the points on the binodal line, where p is maximum, we find for very low temperatures $\frac{v}{b} = \frac{\frac{1}{b}\frac{db}{dx}}{\frac{1}{a}\frac{da}{dx}}$.

In fig. 46 PA represents the first-mentioned locus and PA'

the last-mentioned. As is known from the properties of mixtures with minimum T_k, the point P lies at a value of x for which

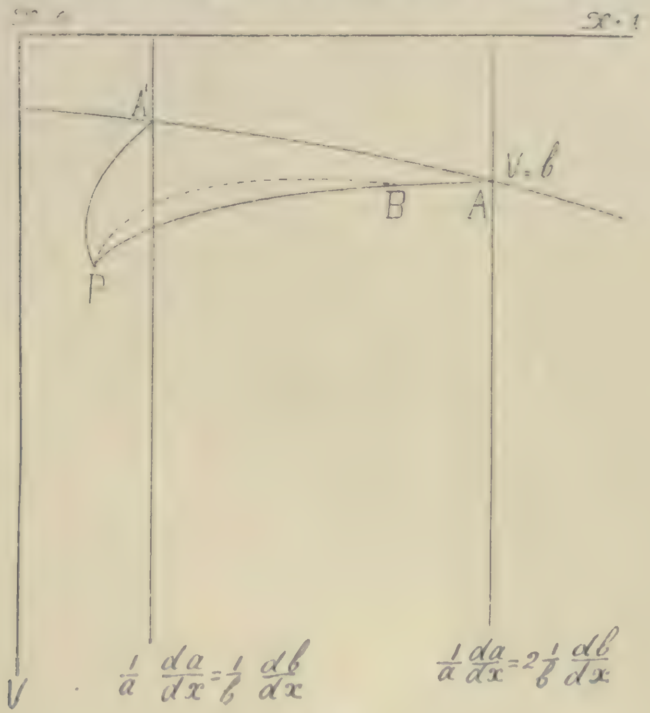
x = 1
A'
V = b
B
A
P
V
$\frac{1}{a}\frac{da}{dx}=\frac{1}{b}\frac{db}{dx}$
$\frac{1}{a}\frac{da}{dx}=2\frac{1}{b}\frac{db}{dx}$

Fig. 46

$\frac{1}{a}\frac{da}{dx}=\frac{2}{3}\frac{1}{b}\frac{db}{dx}$. It is true that I have shown before that if we also take the variability of b with v into account, the factor $\frac{2}{3}$ must be increased. But for our investigation for which we do not lay claim to quantitative accuracy, this is not essential. Let us now also draw the locus of the points where the binodal line is intersected by $\left(\frac{d^2v}{dx^2}\right)_p=0$. At very low temperatures, when v is almost equal to b, the loop of $\left(\frac{d^2v}{dx^2}\right)_p=0$ is either contracted to a single point or has disappeared altogether, as will be the case if b is a quadratic function. But if it originates, it takes place in the neighbourhood of a point of PA. Therefore I have made the dotted line which is the locus of the points in which $\left(\frac{d^2v}{dx^2}\right)_p=0$ intersects the binodal line, start in a point of PA. As may be supposed as known, it also passes through P. That this locus before arriving at P, would also intersect

PA', is not to be expected. If this intersection took place, the demonstrated property only holds at lower temperatures.

In fig. 47 I have represented the T,x-projection of the plaitpoint

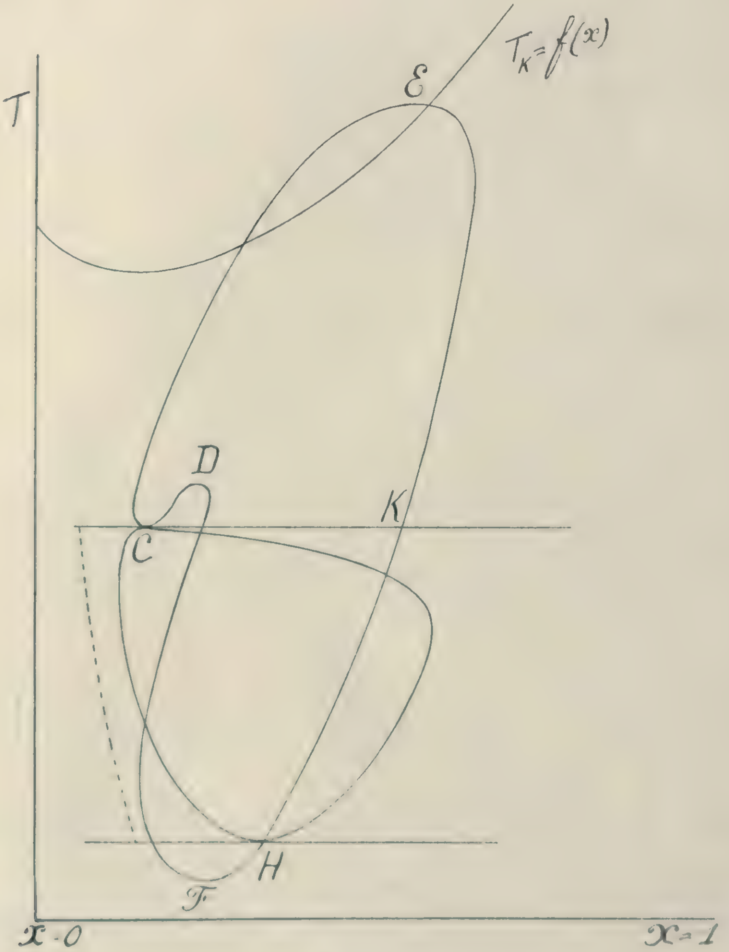

Fig. 47.

line. The point C again indicates the double point of the spinodal line and so also of the binodal line. So at the temperature of C a couple of homogeneous plaitpoints arise. So at higher temperature there are two, the lefthand point of which belongs to the detached closed longitudinal plait, and the righthand point of which remains hidden under the equilibrium liquid—vapour, and vanishes only at the temperature of the point D in consequence of its coinciding with the hidden plaitpoint. At temperatures below T_c, when the longitudinal plait intersects the transverse plait, there is of course a plaitpoint which does not vanish at the same time as the point

C is formed. So here again we meet with a circumstance to which I had directed the attention already before, also in the previous Contribution.

The part CDF yields the whole series of hidden plaitpoints. Here too we have again assumed that not $T=0$ for the point F; but also in the description of this plaitpoint line I have not anxiously questioned whether it can occur for positive ε_1 and ε_2. The line CE contains the plaitpoints of the longitudinal plait which lies closest to the equilibrium liquid-vapour. As we have assumed $\frac{d^2b}{dx^2} > 0$, the point E will lie at the highest temperature at which the longitudinal plait still exists, and at a value of v larger than b. The line EK contains the plaitpoints of the longitudinal plait on the side which is turned towards $v=b$, and at temperatures above T_e and KF these same plaitpoints below T_e. The supposition that the longitudinal plait should not be closed on the side of the small volumes, would therefore, cause the whole line EKF to disappear.

The three-phase-pressure lies between T_e and T_H; the coexisting liquids form a closed curve, and the vapour branch always lies on the left of this curve. This has been drawn thus in accordance with the supposition that also at the lowest temperatures the maximum pressure on the p,x-line will occur, and will not have got hidden under the three-phase-equilibrium. Though I incline to this view, and then the objection which I mentioned in the preceding contribution to the assumption of three-phase-pressure for mixtures with minimum T_k would have been removed, this particularity requires confirmation. The vapour branch has been drawn in such a way that with increase of temperature the value of x becomes larger and approaches the value for which T_k is minimum. The first component has namely the smallest value of b.

Besides in fig. 47 the course of $T_k = f(x)$ and $P_{pl} = F(x)$ has also been represented. The points of intersection of this curve with CEK must not be considered as real points of intersection because the value of p will differ.

And now in conclusion this remark. Just as fig. 39 passes into fig. 40 if we make P_{cd} increase till this point gets in the neighbourhood of $T_k = f(x)$ — fig. 47 will pass into fig. 43 if we make the point C rise, till $T_k = f(x)$ is reached or approached. Whether this is only a mathematical particularity, however, will have to be settled chiefly by experimental data.

Physics. — *"On the course of the isobars in binary systems"* III. By Prof. Dr. PH. KOHNSTAMM. (Communicated by Prof. J. D. VAN DER WAALS.)

18. We showed in § 3 of the first communication (These Proc. of Jan. 1909, p. 599) that the equation $b=0$ has always two real roots: whether the equation $a=0$ will have real roots or not will depend on this whether a^2_{12} is greater or smaller than a_1a_2. We shall get all possible cases for the isobars when we give the line which represents a as function of x (and which we shall briefly call the a-line) all possible positions with respect to the b-line. Let us first investigate the supposition $a^2_{12}<a_1a_2$. We first consider the case that the minimum of the a-line lies on the right side of b_1. (We call the two points where $b=0$, from the right to the left b_1 and b_2, and shall afterwards apply the same notation also for a). Then we have the position of the two lines represented by fig. 18[1]. That in this case there is always a minimum critical temperature, follows from the considerations of § 11. For these teach that $\frac{dT_k}{dx}$ must always be positive for $x=+\infty$, as soon as the minimum of the a-line lies on the righthand of that of the b-line. We need not dwell on the course of the isobars in this case; it is the usual case, further illustrated for low temperatures by the figs. 16 and 17.

If the a-line moves to the left, so that the minimum gets on the left of b_1 but still continues to be on the right of the minimum of the b-line, we shall only notice a difference in the shape of the isobars at lower temperatures. There we shall namely get the course of the figs. 12 and 10 instead of that of fig. 16 or 17 according as the maximum and the minimum of the critical pressure drawn in fig 18 is present or not. At higher temperature — viz. that temperature for which $MRT\frac{db}{dx}=\frac{da}{dx}$ for the point b_1 — the modification in the course of the line $\frac{dp}{dx}=0$ sets in, in consequence of which these figures pass into those of the first case. This transition may take place both above the minimum critical temperature of the system and not above it, hence figures as figs. 13 and 14 will be possible, but it is just as well possible that already before the line

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[1] Cf. preceding communication. In the diagram the minimum of a lies more to the left than we intended; this is, however, not of influence on the course of the other lines.

$\frac{dp}{dv}=0$ splits up, the line $\frac{dp}{dx}=0$ assumes the shape as drawn in fig. 16. This will depend on how far the a-line has been displaced to the left, and the degree in which $\frac{da}{dx}$ increases with x.

If at last the a-line has moved so far to the left, that the minimum has got on the left of that of b, no minimum critical temperature will occur in the system under consideration, however far we may think the diagram of isobars extended, provided not for negative b. We need not give a separate drawing as an illustration for this course, for it is clear that this figure is obtained when fig. 18 is turned 180° round a line $x=C$ as axis. So in the region to be considered no stationary values will occur in the critical pressure.[1]) So we shall have the course of fig. 10 for the isobars at low temperatures. At a temperature of $\frac{27}{32}\frac{a_1+a_2-2a_{12}}{b_1+b_2-2b_{12}}$ a point of intersection of $\frac{dp}{dx}=0$ and $\frac{dp}{dv}=0$ appears, as according to § 10 $\frac{dp}{dx}=0$ enters the stable region at this temperature. So we get the course of fig. 19. At the temperature $\frac{a_1+a_2-2a_{12}}{b_1+b_2-2b_{12}}$ the curve $\frac{dp}{dv}=0$ closes on the

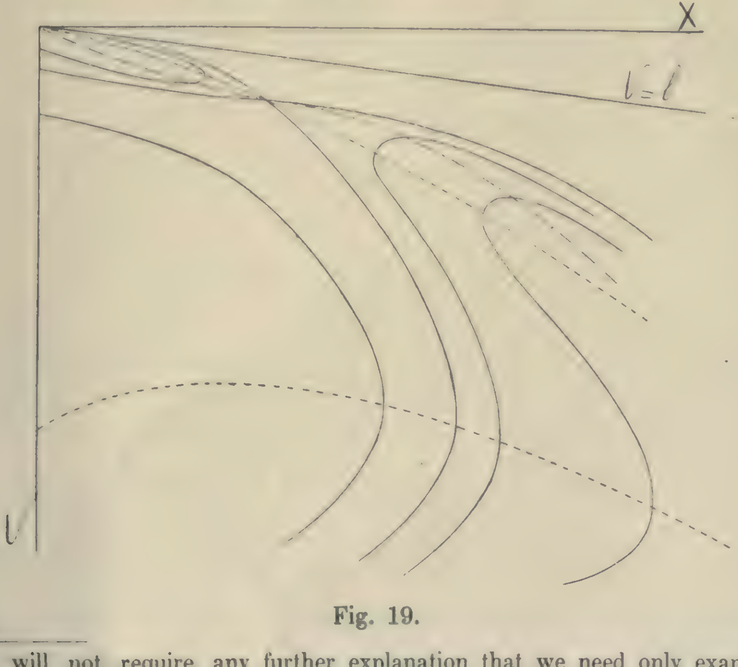

Fig. 19.

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[1]) It will not require any further explanation that we need only examine the portion on the right of the negative b's as we have fixed by definition that b will increase with x.

righthand side and we get the lefthand part of fig. 13 and then fig. 14 or one of the corresponding figures derived from the original figure of isobars of VAN DER WAALS according as we are below or above the temperature for which $MRT\frac{db}{dx}=\frac{da}{dx}$ for the point b_1.

19. Let us now examine the different possibilities ensuing from the supposition $a_{12}^2 > a_1 a_2$. Here we shall have to distinguish a greater number of cases because we have now not only to reckon with the situation of the minimum of the a-line, but also with the two points where $a = 0$. When we think a^2_{12} only little larger than $a_1 a_2$ these points will lie close together, at least closer together than b_1 and b_2.

As first case we assume that a_2 lies on the right of b_1. Fig. 20, which does not call for any further elucidation, shows that in the region of positive a and b no stationary point of T_k and a maximum of p_k occurs. $T_k = 0$ for a_1. So at very low temperature the line $\frac{dp}{dv}=0$ will already be closed on the left side, while a point of intersection of $\frac{dp}{dx}=0$ and $\frac{dp}{dv}=0$ will be found near the x, where p_k becomes maximum. This is in accordance with what we showed in § 10, that viz. for low temperature $\frac{dp}{dx}=0$ lies in the unstable region at very great x. So we get fig. 21 for the course of the isobars, i.e.

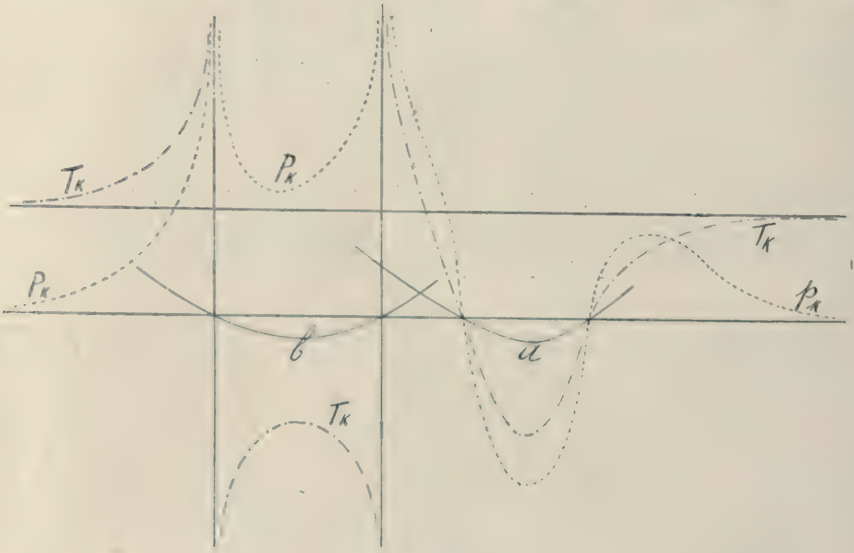

Fig. 20.

the right half of the diagram of isobars of VAN DER WAALS, when we think it drawn above the minimum critical temperature and

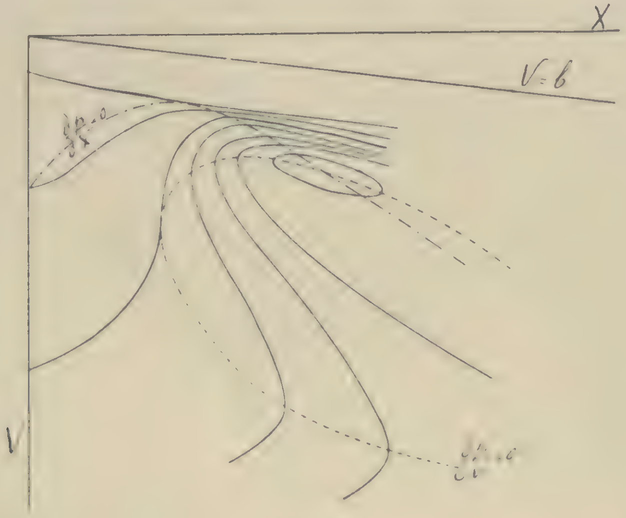

Fig. 21.

below the temperature $\frac{27}{32}\frac{a_1+a_2-2a_{12}}{b_1+b_2-2b_{12}}$ (cf. § 17). At the latter temperature the point of intersection of $\frac{dp}{dx}=0$ and $\frac{dp}{dv}=0$ has vanished, and so also the closed isobars round it; at the temperature $\frac{a_1+a_2-2a_{12}}{b_1+b_2-2b_{12}}$ the line $\frac{dp}{dv}=0$ itself has left the region under consideration moving continually to the right.

2nd *Case*. If the α-line is shifted to the left, we get fig. 22, from which the course of T_k and p_k follows naturally. This case is distinguished from the preceding one only in this, that we get fig. 23 instead of fig. 21 at low temperature. This figure presents a close resemblance to the right half of fig. 13; we have reproduced it separately here to draw attention to the fact that now none of the isobars of high pressure, as is the case in fig. 13, reaches the point $v=0$, $x=x_0$. All the isobars of fig. 23 reach the line $x=x_0$ for a positive value of v. This is in accordance with a remark which we already made in § 8. For in the case now under discussion the α is negative for $x=x_0$ and this involves that $\left(\frac{d^2v}{dx^2}\right)_p<\frac{d^2b}{dx^2}$ for the isobars passing through the point $v=0$, $x=x_0$. So these isobars

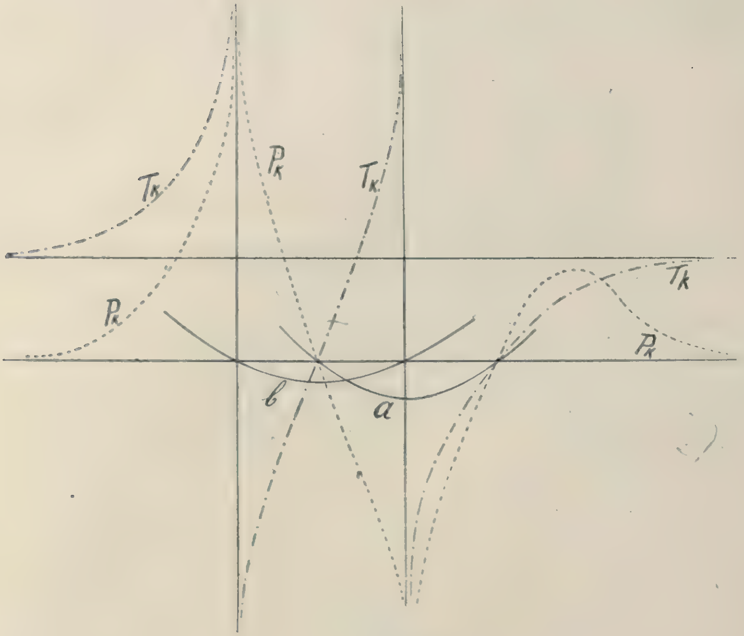

Fig. 22.

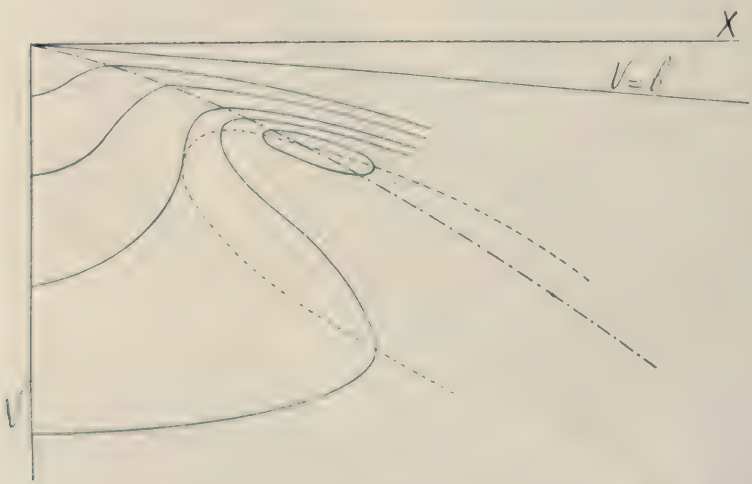

Fig. 23.

run at smaller volumes (for equal x) than $v=b$, and have therefore no physical signification.

3rd *Case.* If the a-line is shifted still more to the left, we obtain fig. 11 with minimum critical temperature, the case fully discussed in the preceding communications. As soon, however, as the minimum of a has got on the left of that of b, we are in the 4th *case.*

The minimum in the critical temperature vanishes again from the region which has physical signification, $\frac{dT_k}{dx}$ becoming negative for $x = +\infty$. We have now decrease of the critical temperature with increase of the size of the molecules. It is again unnecessary to give a separate diagram for T_k and p_k, as the required figure is obtained by revolving fig. 11 180° round an axis $x = C$. At low temperature there is no intersection of $\frac{dp}{dx} = 0$ and $\frac{dp}{dv} = 0$; we have the course of fig. 10. At the temperature $\frac{27}{32} \frac{a_1 + a_2 - 2a_{12}}{b_1 + b_2 - 2b_{12}}$ a point of intersection arises, so we get again fig. 19, which passes again into the left part of fig. 13 and fig. 14. The detaching of $\frac{dp}{dx} = 0$ and $\frac{dp}{dv} = 0$ now always takes place according to fig. 9 in contrast to the other case mentioned for which fig. 19 holds, in which case either fig. 9 or fig. 8 can hold.

5^{th} *and* 6^{th} *cases.* If we think the a-line displaced still more to the left, we get for the course of p_k and T_k the figures originating by turning fig. 22 and fig. 20 180° round an axis $x = C$. For the region of physical signification this course is the same as that of the 4^{th} case, and this holds also for the isobars.

20. If we make a_{12} increase a little more without making this quantity reach the value $\frac{1}{2}(a_1 + a_2)$ the points a_1 and a_2 will move further apart. If the distance between them has become greater than that between b_1 and b_2, it is clear that the situation of the third and the fourth case of the preceding § is no longer possible. Instead of fig. 22 we get then fig. 24, which, however, presents the same thing as fig. 22 in the region on the right of a_1, and so leads to the same results. A new feature, however, appears when we think the a-line still somewhat more displaced to the left, or in other words if we think fig. 24 rotated over 180°. For the minimum of a now lying on the left of that of b, $\frac{dT_k}{dx}$ becomes negative for $x = +\infty$, and so a maximum of T_k must appear, a circumstance, which I think had up to now been always considered as inseparably bound to a negative value of $a_1 + a_2 - 2a_{12}$.

Of course the diagram of isobars will undergo a modification also now; it will constitute the transition to the figure holding for a

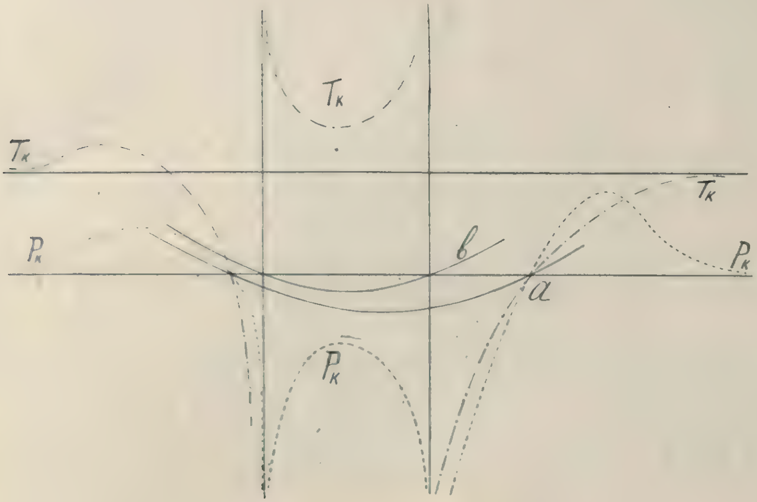

Fig. 24.

negative value of $a_1 + a_2 - 2a_{12}$, which is derived from VAN DER WAALS' diagram of isobars by making the points of intersection of $\frac{dp}{dx} = 0$ and $\frac{dp}{dv} = 0$ interchange their rôles of isolated point and double point (Cf. VAN DER WAALS These Proc. IX p. 629). But so long as the experiment has not given us any case of maximum plaitpoint temperature, it does not seem desirable to me to dwell any longer on this. For it follows immediately from this that in all the examined cases certainly no maximum critical temperature of the mixture taken as homogeneous can occur. In this respect the circumstances for a maximum differ from those for a minimum. As VAN DER WAALS already observed (These Proc. XI p. 157) a minimum value of $\frac{a}{b}$ need not necessarily be attended by a minimum plaitpoint temperature. It might be that above the minimum T_k the plait continues to exist for a long time till in the meantime the point that indicates the critical temperature of the mixture taken as homogeneous has reached $x = 0$ or $x = 1$, a case which is not to be considered as impossible especially when the minimum T_k is to be found very near one of these values. But when there is a maximum T_k, i. e. when at the higher of the two critical temperatures of the pure substances there are still mixtures which are below their T_k, there are sure to be still mixtures which are below their plaitpoint temperature, and so there will be a maximum plaitpoint temperature. This in connection with the fact that the limits of the coexisting phases and of the unstability are always further apart for the real mixture than those for the mixture taken as homogeneous, except for the case $x_1 = x_2$, in which case they coincide. So long, therefore, as not a single mixture has been found with a maximum plaitpoint temperature, it is unnecessary to examine the different cases for the course of the isobars, with which a maximum T_k might be accompanied.

In § 10 we have mentioned a number of points in which the supposition that b is a quadratic function of x is distinguished from the supposition of a linear function. After the foregoing it will, however, be easy to apply in the given figures for the course of the isobars the comparatively slight modifications which would be the consequence of this second supposition.

Physics. — "*On the phenomena of condensation for mixtures of carbonic acid and urethane, in connection with double retrograde condensation.*" By Prof. PH. KOHNSTAMM and J. CHR. REEDERS. (Communicated by Prof. J. D. VAN DER WAALS).

In these Proceedings of March 27th 1909, p. 816 VAN DER WAALS showed that under certain circumstances the phenomenon of double retrograde condensation must occur. We have set ourselves the task to test this result of the theory by the experiment. For this purpose we chose carbonic acid and urethane as a first system. For according to BÜCHNER [1]) a solution of 4 % [2]) urethane splits up into two layers at 30°.5 [3]), and according to p. 29 loc. cit. the succession of the phases is GL_1L_2 [4]). So the three-phase-pressure will certainly exist above the critical temperature of carbonic acid, and also the second condition mentioned by VAN DER WAALS, is fulfilled.

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[1]) Thesis for the doctorate, Amsterdam 1905, p. 113.

[2]) Percentage by weight according to an oral communication from Dr. BÜCHNER.

[3]) This temperature depends, of course, on the degree of filling of the sealed tube used, and the pressure in the tube which depends on this; it does not imply by any means, that a mixture of 4 percentages by weight of urethane could not split up below 30°.5. Compare the table of three-phase-pressures at the end of this communication.

[4]) It is not quite clear on what ground BÜCHNER arrives at this conclusion; it does not follow from his experiments, as it seems to us. But it is undoubtedly plausible to assume that the gas phase consists here of almost pure carbonic acid, which will really appear to be the case. We may point out in passing that the existence of a lower critical point of mixing to which BÜCHNER concludes on p. 113, is proved neither by BÜCHNER's experiments nor by ours. As this point is not to be reached directly (we too always found crystallisation of the urethane), this would only be possible by an accurate investigation of the change of x_2 and x_3 with the temperature.

Our carbonic acid was prepared from commercial carbonic acid by a process of drying by means of P_2O_5, of condensing by liquid air, and of removing the volatile components (air) by blowing off at low temperature. For the urethane we used commercial urethane; the quantity of it being so small compared with that of the carbonic acid, it seemed superfluous to purify it further.

As it is of the highest importance in these experiments, as will appear, to regulate the concentration of the mixture very accurately, we must give a description of the way in which our Cailletet tubes were filled. A quantity of urethane shaped into a rod by melted urethane being sucked up in a capillary tube, was weighed off (once we used about 15 mg., the other times about 5 mg.). The rod was put in a Cailletet tube and spread over the wall by being melted; after a stirrer had been applied the tube was placed in a pressure cylinder as usually; then the mercury was pumped up in the tube so as fill it half, and then the cock which led to the pump, was closed so that the mercury got a constant position. The Cailletet tube passed into a narrow capillary at the upper end, to which a steel capillary was fastened by means of sealing-wax, which led to a steel high pressure cock of a model specially prepared with a view to quantitative conveyance of measured gas quantities for the Amsterdam Laboratory by the firm SCHÄFFER and BUDENBERG. The two requirements (apart from the ordinary requirements which are in connection with perfect closure) which such a cock must fulfil, are: 1. Absence of all recesses or places where gas might be left behind. 2. Absence of all that might contaminate the passing gas. The model represented in fig. 1 meets both requirements, as all packing material has been avoided for the joints of the leading tubes *A* and *B*. A steel cone *C*, which is soldered [1]) to the leading capillary tube is tightly pressed against the conical wall of the cock by the nut *D*, and thus forms a perfectly tight closure of steel on steel. As the borings of the cock are made perpendicular to each other, in which care is taken that when the horizontal boring is being made, the borer does not penetrate into the wall of the vertical one, a cock is obtained, in which the gas finds nowhere an opportunity of entering a recess from which it cannot be removed by mercury. Of course the cock must be used in a vertical position, i. e. with the pivot *E* turned upwards and the cavity *F* turned downwards as indicated in the

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[1]) To prevent the solder from being attacked by the mercury a raised rim is left when the steel conus *C* is pierced (see fig.), against which the capillary is tightly pressed. So the solder which is poured between the capillary and the cone cannot come into contact with the mercury.

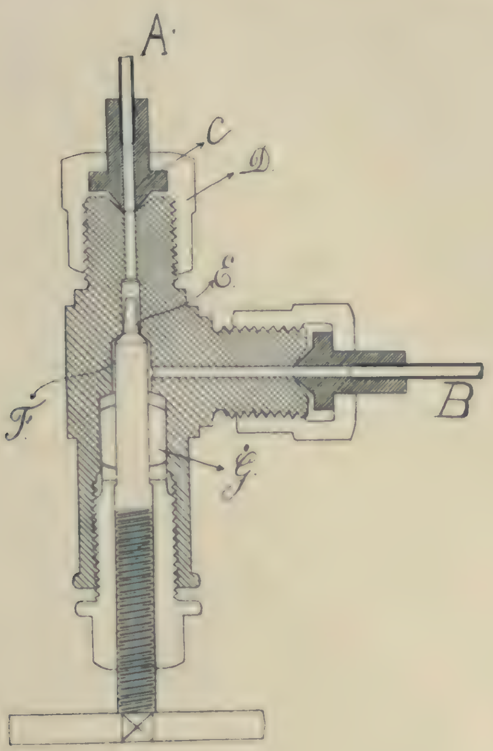

Fig. 1.

figure. The cock being filled with mercury before use, the cavity *F* is filled with mercury up to the horizontal tube, and the passing gas is thus entirely shut off from the inevitable packing material at *G*. The handling of these cocks is greatly facilitated by the construction of the pivot *E*. Instead of consisting in a single cone, as it generally does, it consists in a broader cone, which terminates at the top in a very steep, truncated cone, which is almost as wide as the bore of the cock. In this way we achieve that when turning the handle, the opening only very slowly increases, which renders a very fine regulation possible. Particularly when first mercury is to pass through the cock, and then gas which has much less friction (this takes place in different manipulations see below, p. 916) it is of great importance that the width of the opening can be very accurately regulated.

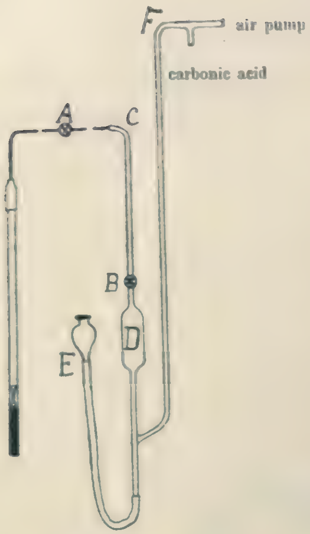

Fig. 2.

By means of such a cock (A, fig. 2) and the glass cock B the Cailletet tube is in connection with the calibrated space D, which according as the mercury reservoir E is raised or lowered, is closed by mercury or is brought in connection with the tube F, which leads with a T-joint to the airpump and the carbonic acid reservoir. We now start with exhausting the whole space, then close B and introduce a quantity of carbonic acid into D, which is measured by the difference in pressure in D and F, and the temperature of the waterbath, in which D is found (omitted in the figure). Now the Cailletet tube is cooled by means of liquid air 1) and the cock B opened, which causes all the carbonic acid to be distilled over, and the whole conduit C, with the cock A and the steel and glass capillary to be filled with mercury in consequence of the diminished pressure. To prevent the mercury from filling the whole Cailletet tube, the glass capillary 2) has also been cooled with liquid air, so that the mercury congeals in it, and does not fall. Now A is closed and the carbonic acid thawed. To prevent the mercury from no longer adhering to the steel and the glass capillary and from falling in consequence, it is kept frozen in the glass capillary till the carbonic acid is thawed, and a sufficient pressure in the tube is ensured. As it is very easy to enclose a desired quantity of carbonic acid by regulating the pressure in the measuring vessel D, we can in this way easily obtain every required concentration with great accuracy. Moreover this arrangement has the advantage that we can increase or decrease the quantity of carbonic acid without being obliged to take the apparatus to pieces. To admit more carbonic acid we have only to open A very slowly so that the compressed gas drives the mercury before it almost to the cock B; then A is closed again. We then measure the required quantity in D, join the two quantities of carbonic acid, which are still separated by the mercury above B, to each other, and lead all the carbonic acid into

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1) With a view to these repeated great refrigerations the Cailletet tube has been made of borosilicate glass (Schott 59 III); bursting of these tubes hardly ever occurs.

2) Not before all the carbonic acid has passed, to prevent the capillary from being stopped.

the Cailletet tube as above. If we wish to diminish the quantity of carbonic acid, we leave A, after it has been carefully opened, open till the vessel D has filled with carbonic acid under the desired pressure. We then close the two cocks, exhaust D, and deliver the carbonic acid above B again into the Cailletet tube.

The further method of observation does not call for a detailed discussion. We shall only remark that the temperature was obtained by an ordinary waterbath with toluol regulator, and the pressure measured with a spring manometer of the model constructed by SCHÄFFER & BUDENBERG for accurate measurements for the Amsterdam Laboratory. As we intend shortly to publish a separate communication on the experiences with these instruments, it may suffice here to state that they are excellently adapted to reach the required accuracy of no more than 0.1 per cent, provided they are used in connection with a pressure-balance which enables us to test them from time to time with very little trouble.

As a first mixture we investigated a mixture of the concentration $x = 0.042$. It appeared already at the outset that the system urethane-carbonic acid fulfils the condition that at equal temperature the three-phase-pressure lies below the pressure of saturation of carbonic acid. For a temperature of 26°.1 we find a three-phase-pressure of 65.15 Kg. per cM^2. = 62.95 atms., while KEESOM gives 64.4 atms. as pressure of saturation for 25°.55. At 32°.05 we found 74.35 Kg. per cm^2 = 71.85 atms. KEESOM gives 72.93 for 30°.98 (critical point). The purity of the prepared mixture appeared from the constancy of the three-phase-pressure which from the beginning to the end of the existence of the three phases only increased about 0.25 Kg. per cm^2. Also for the other mixtures to be discussed presently this condition was fulfilled. Perhaps even a better warrant of the absence of impurities (air) was furnished by the fact that the different values for the three-phase-pressure obtained for different mixtures at the same temperature, harmonized perfectly. Thus we found:

				Kg. per cM.^{2}		
at 31°.9 for mixture	I	74.10	mixture III	74.20	IV	74.20[1]
34 .9	III	79.15	VI	79.10		
35 .9	I	80.80	III	80.85	VI	80.85
37 .1	II	82.85	III	82.80		

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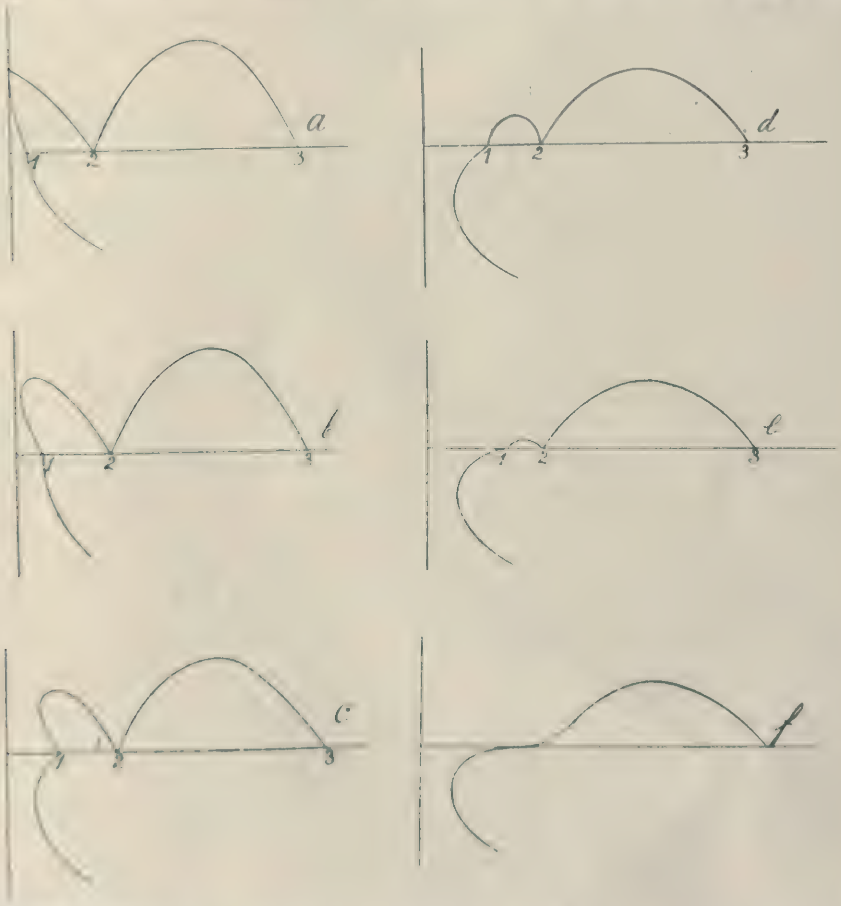
[1] Cf. the table containing all the three-phase-pressures noted down by us. They always give the mean value, i. e. the value for which none of the three phases has almost disappeared. In the text we have taken those values for a comparison which could be reduced to the same temperature with the slightest inter-, or extrapolation, in which 0.15 increase per 0°.1 is assumed. But also for nearly

But at the same time this mixture taught us that we had taken the concentration still much too great. For with increase of the pressure the topmost of the three phases always disappeared first, so that two liquid layers remained. Instead of on the left side of the point 1 of VAN DER WAALS' fig. 41, (which we reproduce below) as is required for the observation of the double retrograde condensation, we were all the time on the right side of the point 2. This appeared also to be the case, at least for higher temperature (I regret to say that we have neglected to observe this condensation at the lowest temperature to be reached before the solid substance makes its appearance) with the mixture II of concentration $x = 0.0245$. With this mixture we determined the point of maximum three-phase-pressure, i. e. the point, at which in the presence of the third, dense phase



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all the other values a similar concordance is found by interpolation, except for the three placed between parentheses in which the stirring has apparently not been sufficient to reach complete equilibrium, or for which another error of observation made itself felt.

the meniscus vanishes between the two other phases in the middle of the tube under critical phenomena. So it is this temperature and pressure which are indicated by fig. *f*. These appeared to be 37°.3 and 83.15 Kg. per cM^2. The x of the point with horizontal tangent is, therefore, smaller than 0.0245.

As mixture III taught us, however, this x is greater than 0.0100. For this mixture of the concentration mentioned yielded the three-phase-pressures mentioned in the table up to 37°.1, but at 37°.2 three-phase-pressure was no more observed. The dense liquid (3), (which distinguished itself so greatly from the other liquid by its viscosity, colour, and refractivity that they could not possibly be confounded) which formed already at very low pressure, increased to a maximum, then decreased, and had entirely disappeared at 83.00. Then the mixture remained homogeneous up to the highest attainable pressures. So at 37°.2 and $x = 0.0100$ we are clearly in the case of fig. *e*, on the left side of 1. At 37°.1, however, three-phase-pressure appeared again, so the point 1 moves from left to right between 37°.1 and 37°.2 past the concentration $x = 0.01$. At 37°.2 no double retrograde condensation can, of course, be observed, because then the line for the equilibrium 1, 2 no longer inclines to the left, which is by no means astonishing, as it has already entirely disappeared 0°.1 higher. The point with horizontal tangent of fig. *f* lies, therefore, evidently between $x = 0.0100$ and $x = 0.0245$, and that probably much closer to the first-mentioned than to the last-mentioned value, as already at 37°.1 with increase of the pressure the meniscus disappears in the top of the tube, i.e. the plaitpoint lies already on the left side of $x = 0.0100$.

As a fourth mixture ($x = 0.00765$) did not reveal anything new, we immediately passed on to a fifth of $x = 0.00540$ and then to a sixth of $x = 0.00375$. In both we could very clearly ascertain the retrograde condensation of the dense liquid observed already for the third mixture, but we did not succeed in finding double retrogade condensation. For in order not to get on the line of the three-phase-pressure, the temperature had even to be raised above 36°.15 for the mixture of $x = 0.00375$. Then, however, after the dense liquid had disappeared everything remained homogeneous up to the highest pressures. At 36°.10 the three-phase-pressure reappeared. The point 1 of figure *d*, where the tangent to the branch plait is vertical for the three-phase-pressure is, therefore, still on the left of 0.00375. We have resolved, at least for the present, not to continue our investigations at still smaller x. Not because the preparation of such mixtures would give rise to difficulties, in the way described we shall easily be able to reach the value 0.001 and smaller. But the maximum quantity of the dense liquid, which was even difficult to observe for our last mixture, gets so small at still smaller x that it is lost to sight. Already for quantities as they are found in our mixture VI we were in danger of being misled about the appearance of the homogeneous state by the exceedingly slight quantity of liquid being spead over the wall of the tube by the stirring, which is necessary for the equilibrium. Only when after violent stirring we waited a long time, we saw a trace of liquid slowly collect again on the bottom of the tube. Perhaps we may succeed by special experimental contrivances (e.g. by increasing the quantity of substance without enlarging the wall of the tube in the same proportion nor the diameter of the tube at the place where the liquid collects) to surmount this difficulty. For the present we prefer to try and ascertain the double retrogade condensation in other systems where it may not take place with such a small x as in the investigated one. As such, systems of ethane and nitrous oxyde with little volatile substances suggest themselves in the first place.

If the phenomena described up to now are in perfect concordance with the theoretical anticipations — and not the least in this that double retrograde condensation is a phenomenon exceedingly difficult to observe — in one respect the obtained experimental result was different from what we had expected. On p. 825 loc. cit. VAN DER WAALS says: "We might begin to try and show that after the termination of the first retrograde condensation of the equilibrium 3.1 another condensation makes its appearance with further raised pressure." This sentence and the preceding one: "The fact that it only undoubtedly exists for such small values of x which do not only lie below x_1 but must moreover be smaller than the value of x of the plaitpoint of the equilibrium 2.1 etc.", suppose — a supposition which naturally suggests itself — that it will be comparatively easy to realise the retrograde condensation of the second liquid, but very difficult to realise the circumstances in which after this the condensation of the lighter liquid takes place in a retrograde way. To our surprise it appeared, however, that for the condensation 2.1 the retrograde phenomenon appears with a distinctness as is only met with for very concentrated mixtures as a rule. Not only did it appear that for the mixture $x = 0.00375$ the point of contact and the plaitpoint were still about 1°.65 apart (or more; the plaitpoint lay at 34°.5, and it is the question whether we have really reached the temperature of the point of contact, this may remain in the metastable region); but also the increase of the liquid, which may be obtained in a very large quantity, and its subsequent decrease, were to be ascertained with exceeding clearness. This may be in connection with the fact that in this case the p,x-loop is very steep and very narrow, so that comparatively high above the plaitpoint still a very great quantity of liquid is to be found. At any rate these phenomena prove again, how enormous an influence a small quantity of admixture may have on the behaviour of a substance. A quantity of not quite $0.4^{\circ}/_{0}$ admixture first gives three-phase-pressure, then a very pronounced retrograde condensation, and thus modifies the phenomena of condensation of the pure carbonic acid altogether.

THREE-PHASE-PRESSURES OF THE SYSTEM URETHANE-CARBONIC ACID.
(The Roman figures denote with which of the above-mentioned mixtures the determination was made).

T	p KG per cm.^{2}	Mixture	T	p KG per cm.^{2}	Mixture
26°.1	65.15	I	34°.5	78.30	V
28°.9	69.55	IV	34.9	79.10	VI
(29.7)	(70.35)	V	34.9	79.15	III
(31.6)	(73.35)	III	35.25	79.85	V
31.7	73.85	V	35.8	80.65	III
31.8	74.05	V	35.85	80.80	VI
31.9	74.20	III	36.1	81.20	VI
32.05	74.35	I	36.6	82.30	III
(32.05)	(74.20)	III	37.1	82.80	III
32.4	75.00	V	37.3	83.15	II Maximum
33.0	75.70	III			
33.4	76.30	V			
33.95	77.35	III			

Amsterdam. *Physical Laboratory of the University.*

(May 24, 1909).

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